

# CHAPTER 8

---

## Halocarbon Scenarios, Ozone Depletion Potentials, and Global Warming Potentials

**Lead Authors:**

J.S. Daniel  
G.J.M. Velders

**Coauthors:**

A.R. Douglass  
P.M.D. Forster  
D.A. Hauglustaine  
I.S.A. Isaksen  
L.J.M. Kuijpers  
A. McCulloch  
T.J. Wallington

**Contributors:**

P. Ashford  
S.A. Montzka  
P.A. Newman  
D.W. Waugh



# CHAPTER 8

## HALOCARBON SCENARIOS, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS

### Contents

SCIENTIFIC SUMMARY .....	8.1
8.1 INTRODUCTION .....	8.5
8.2 HALOCARBON LIFETIMES, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS .....	8.5
8.2.1 Introduction .....	8.5
8.2.2 Ozone Depletion Potentials .....	8.5
8.2.2.1 Atmospheric Lifetimes .....	8.6
8.2.2.2 Fractional Release Factors .....	8.6
8.2.2.3 Ozone Destruction Effectiveness .....	8.7
8.2.2.4 ODP Values .....	8.8
8.2.3 Direct Global Warming Potentials .....	8.8
8.2.4 Degradation Products and Their Implications for ODPs and GWPs .....	8.13
8.3 FUTURE HALOCARBON SOURCE GAS CONCENTRATIONS .....	8.13
8.3.1 Introduction .....	8.13
8.3.2 Baseline Scenario (A1) .....	8.15
8.3.2.1 Emissions .....	8.15
8.3.2.2 Mixing Ratios .....	8.21
8.3.2.3 Equivalent Effective Stratospheric Chlorine .....	8.25
8.3.3 Alternative Projections .....	8.28
8.3.3.1 Emissions .....	8.28
8.3.3.2 Mixing Ratios .....	8.28
8.3.3.3 Equivalent Effective Stratospheric Chlorine .....	8.30
8.3.4 Uncertainties in ODS Projections .....	8.32
8.4 OTHER PROCESSES RELEVANT TO FUTURE OZONE EVOLUTION .....	8.34
8.5 INDIRECT GWPS .....	8.35
REFERENCES .....	8.36



## SCIENTIFIC SUMMARY

## Ozone Depletion Potentials and Global Warming Potentials

- **The effectiveness of bromine compared with chlorine on a per-atom basis for global ozone depletion, typically referred to as  $\alpha$ , has been re-evaluated upward from 45 to a value of 60.** The calculated values from three independent two-dimensional models range between 57 and 73, depending on the model used and depending on the assumed amount of additional bromine added to the stratosphere by very short-lived substances (VSLs).
- **Semi-empirical Ozone Depletion Potentials (ODPs) have been re-evaluated, with the most significant change being a 33% increase for bromocarbons due to the update in the estimate for the value of  $\alpha$ .** A calculation error in the previous Assessment, which led to a 13% overestimate in the halon-1211 ODP, has been corrected.
- **Direct Global Warming Potentials (GWPs) have been updated to account for revised radiative efficiencies (HFC-134a, carbon tetrafluoride (CF<sub>4</sub>), HFC-23, HFC-32, HFC-227ea, and nitrogen trifluoride (NF<sub>3</sub>)) and revised lifetimes (trifluoromethylsulfurhexafluoride (SF<sub>5</sub>CF<sub>3</sub>) and methyl chloride (CH<sub>3</sub>Cl)).** In addition, the direct GWPs for all compounds have been affected by slight decreases in the carbon dioxide (CO<sub>2</sub>) absolute Global Warming Potentials for various time horizons.
- **Indirect GWPs have been updated primarily to reflect the later return of ozone-depleting substances (ODSs) to 1980 levels estimated in this Assessment and to account for the increased bromine efficiency factor.** Direct and indirect GWPs are presented separately due to concern over the appropriateness of combining them into net GWPs for application in certain climate change issues.

## Projections of Halocarbon Abundances and Implications for Policy Formulation

- **Several of the options evaluated for accelerating the future reduction of ODS abundances demonstrate greater effectiveness than assessed previously.** These options are assessed using equivalent effective stratospheric chlorine (EESC) derived from projections of the atmospheric abundances of ODSs based on historic emissions, observations of concentrations, reported production, estimates of future production, and newly available estimates of the quantities of ODSs present in products in 2002 and 2015.
- **The date when EESC relevant to midlatitude ozone depletion returns to pre-1980 levels is 2049 for the baseline (A1) scenario, about 5 years later than projected in the previous Assessment.** This later return is primarily due to higher estimated future emissions of CFC-11, CFC-12, and HCFC-22. The increase in CFC emissions is due to larger estimated current bank sizes, while the increase in HCFC-22 emissions is due to larger estimated future production.
- **For the polar vortex regions, the return of EESC to pre-1980 conditions is projected to occur around 2065, more than 15 years later than the return of midlatitude EESC to pre-1980 abundances.** This later return is due to the older age of air in the lower stratosphere inside the polar vortex regions. This metric for the polar vortex regions has not been presented in previous ozone Assessments.
- **Three classes of hypothetical cases are presented here to illustrate the maximum potential for reducing midlatitude EESC if anthropogenic production or emission were eliminated after 2006 and if the existing banks at the end of 2006 were fully eliminated.** The sizes of the banks considered for elimination are equal to the total estimated production through 2006 minus all estimated emissions through 2006. These cases are not mutually exclusive, and separate effects of the elimination of production, emissions, and banks are not additive.

The table below shows the percentage reductions in integrated EESC relative to the baseline (A1) scenario that can be achieved in these hypothetical cases (see table footnote 1). EESC is integrated above the 1980 level from 2007 until it returns to the 1980 level (about 2050), and any potential contribution from VSLs is neglected.

## HALOCARBON SCENARIOS, ODPs, AND GWPs

Compound or Compound Group	Reduction in Integrated EESC Relative to Baseline Scenario A1 (%)		
	Hypothetical Case A: All Emissions Eliminated from Production after 2006	Hypothetical Case B: All Emissions Eliminated from Existing Banks at End of 2006	Hypothetical Case C: All Emissions Eliminated after 2006
CFCs	0.3	11	11
Halons	0.5	14	14
CCl <sub>4</sub>	3	(a)	3
CH <sub>3</sub> CCl <sub>3</sub>	0.2	(a)	0.2
HCFCs	12	4	16
CH <sub>3</sub> Br (anthropogenic)	5	(a)	5

<sup>1</sup> Hypothetical case A corresponds to the elimination of all emissions from production after 2006. Hypothetical case B corresponds to the elimination of all emissions from banks existing at the end of 2006 (for example, capture and destruction). Hypothetical case C corresponds to the elimination of all emissions after 2006 and is approximately equal to the sum of columns A and B.

(a) For these compounds, banks are uncertain and therefore emissions are equated to production in these calculations.

- **The percentage reductions in EESC for halons and CFCs, integrated from 2007 until the 1980 level is reattained (shown in column B), are larger than previously reported.** This is because recent bank estimates from the Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (IPCC/TEAP) 2005 Special Report are significantly larger and likely more reliable than values presented in previous Assessments for CFC-11, CFC-12, and halon-1211.
- **The percentage reductions in integrated EESC for HCFCs shown in hypothetical case A are larger than previously reported.** This is because of significantly larger estimates of future HCFC-22 production in Article-5 countries.
- **Evidence suggests that anthropogenic emissions have a stronger influence on atmospheric mixing ratios of CH<sub>3</sub>Br than reported in the previous Assessment.** This enhanced sensitivity leads to a greater impact of an elimination of these emissions on EESC. The effect of an elimination of the anthropogenic methyl bromide emission on integrated EESC is about 50% larger than it would have been if the same fractional anthropogenic emission were used as was assumed in the previous Assessment.
- **The hypothetical elimination of all emissions of ODSs after 2006 (hypothetical case C) would accelerate the year EESC is expected to drop below the 1980 value by about 15 years, from 2049 to 2034.** The hypothetical elimination of all emissions from production of ODSs after 2006 (hypothetical case A) would accelerate it by about 6 years, to 2043.
- **Two additional hypothetical cases of critical and exempted (quarantine and pre-shipment, QPS) uses of methyl bromide were considered.** In the analysis of both cases, EESC is integrated above the 1980 level from 2007 until it returns to the 1980 level. A methyl bromide phase-out has been in effect since 2005 in developed countries, with critical-use exemptions granted in 2005 and 2006 at levels that are 30-40% of the 2003-2004 production levels. The size of the critical-use exemptions is similar to the estimated use of methyl bromide for QPS use.
  - **If critical-use exemptions continue indefinitely at the 2006 level compared with a cessation of these exemptions in 2010 or 2015, midlatitude integrated EESC would increase by 4.7% or 4.0%, respectively.**

- If production of methyl bromide for QPS use were to continue at present levels and cease in 2015, mid-latitude integrated EESC would decrease by 3.2% compared with the case of continued production at present levels.

### Uncertainties and Sensitivities

- **Recent bank estimates from the IPCC/TEAP (2005) report are significantly larger and likely more reliable than values presented in previous Assessments for some compounds (CFC-11, CFC-12, halon-1211, and halon-1301).** However, there remain potential shortcomings in these new bank estimates that lead to uncertainties in assessing the potential for reducing integrated future EESC.
- **While the future evolution of the ozone layer depends largely on the abundances of ozone-depleting substances, changes in climate arising from natural and anthropogenic causes are likely to also play an important role.** Many of these changes are expected to induce spatially dependent chemical and dynamical perturbations to the atmosphere (Chapters 5 and 6), which could cause ozone to return to 1980 levels earlier or later than when EESC returns to 1980 levels. Furthermore, the changes may alter the lifetimes of the important ozone-depleting substances.



## 8.1 INTRODUCTION

This chapter provides an update of future halocarbon mixing ratio estimates and of Ozone Depletion Potentials and Global Warming Potentials. Future scenarios of halocarbons are constructed based on the current Montreal Protocol and build on the previous Scientific Assessments of Ozone Depletion (WMO, 1999, 2003) and on the recently published Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (IPCC/TEAP) Special Report on *Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons* (IPCC/TEAP, 2005). A number of hypothetical cases are presented to demonstrate how halocarbon production and emission, and halocarbons present in current applications, may contribute to the future ozone-depleting substance (ODS) loading of the atmosphere. Uncertainties in future emissions and atmospheric concentrations are discussed, as are the important differences from previous Assessments.

## 8.2 HALOCARBON LIFETIMES, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS

### 8.2.1 Introduction

Halocarbons released from the Earth's surface become mixed in the lower atmosphere and are transported into the stratosphere by normal air circulation patterns. They are removed from the atmosphere by photolysis, reaction with hydroxyl (OH) radicals (for compounds containing carbon-hydrogen bonds), and for some compounds, uptake by the oceans. Halocarbon molecules that are transported to the stratosphere deposit their degradation products directly. A small fraction of the degradation products from halocarbons destroyed before leaving the troposphere can also be transported to the stratosphere (see Chapter 2). The final degradation products are inorganic halogen species containing fluorine, chlorine, bromine, and iodine atoms. A significant fraction of inorganic chlorine, bromine, and iodine are in the form of X (X = Cl, Br, or I) and XO that participate in efficient ozone destruction in the stratosphere. Fluorine atoms, in contrast, are rapidly converted into hydrogen fluoride (HF), which is a stable reservoir and prevents fluorine from contributing to ozone destruction to any significant degree. Iodine atoms participate in catalytic ozone destruction cycles, but rapid tropospheric loss of iodine-containing compounds limits the amount of iodine reaching the stratosphere (see Chapter 2).

All halocarbons also absorb terrestrial radiation (long-wavelength infrared radiation emitted from the

Earth's surface and by the atmosphere) and contribute to the radiative forcing of climate change. The relative contribution of individual compounds to stratospheric ozone depletion and global warming can be characterized by their Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs), respectively. ODPs and GWPs have been used in past ozone and climate Assessments (IPCC, 1990; 1995; 1996; 2001; 2005; WMO, 1995; 1999; 2003) and in international agreements such as the Montreal Protocol and the Kyoto Protocol.

### 8.2.2 Ozone Depletion Potentials

Ozone Depletion Potentials are indices that provide a simple way to compare the relative ability of various ODSs to destroy stratospheric ozone (Fisher et al., 1990; Solomon et al., 1992; Wuebbles, 1983). The concept of the ODP has been discussed extensively in previous WMO reports (WMO, 1995; 1999; 2003). ODPs are often calculated assuming steady-state conditions with constant emissions (for compounds that are removed by linear processes, this is equivalent to assuming an emission pulse and integrating over the entire decay of the compound (Prather, 1996; Prather, 2002)) and are not dependent on time. Time-dependent ODPs can also be calculated (Solomon and Albritton, 1992), which reflect the different time scales over which the compound and reference gas (the chlorofluorocarbon CFC-11) liberate chlorine and bromine into the stratosphere. Compounds that have shorter (longer) atmospheric lifetimes than CFC-11 have ODPs that decrease (increase) with increasing integration time.

The ODPs considered here are steady-state ODPs, integrated quantities that are distinct for each halocarbon species. The ODP of a well-mixed ozone-destroying species  $i$  is given by:

$$\text{ODP}_i = \frac{\text{global O}_3 \text{ loss due to unit mass emission of } i}{\text{global O}_3 \text{ loss due to unit mass emission of CFC-11}} \quad (8-1)$$

This quantity can be calculated using computer models, with the accuracy depending on the model's ability to simulate the distribution of the considered halocarbon and the ozone loss associated with it. Because ODPs are defined relative to the ozone loss caused by CFC-11, the ODP values demonstrate less sensitivity to photochemical modeling errors than do absolute ozone loss calculations.

Taking advantage of this reduced sensitivity, Solomon et al. (1992) proposed a semi-empirical approach to estimate ODPs that approximates and simplifies the accurate representation of ozone photochemistry and provides an observational constraint to the model-based

## HALOCARBON SCENARIOS, ODPs, AND GWPs

results. In this approach, measurements of correlations between halocarbons are used to evaluate chlorine and bromine relative stratospheric release values. These release rates are used with lifetimes, molecular weights, and the number and type of halogen atoms per molecule to estimate the effect of a small source gas pulse emission on stratospheric ozone depletion. In the case of bromine and iodine, the catalytic efficiency for ozone destruction relative to chlorine is needed and differs from unity partly due to the different partitioning of the halogen chemical families. For long-lived chlorocarbons and bromocarbons that are well mixed in the troposphere, the semi-empirical ODP definition can be expressed by:

$$ODP_i = (\alpha n_{Br,i} + n_{Cl,i}) \frac{f_i}{f_{CFC-11}} \frac{\tau_i}{\tau_{CFC-11}} \frac{M_{CFC-11}}{M_i} \frac{1}{3} \quad (8-2)$$

where  $f$  is the fractional halogen release factor,  $\alpha$  is the relative effectiveness of bromine compared with chlorine for ozone destruction,  $\tau$  is the global lifetime,  $M$  is the molecular weight, and  $n_{Cl}$  ( $n_{Br}$ ) is the number of chlorine (bromine) atoms contained in the compound. *CFC-11* subscripts indicate quantities for CFC-11, while  $i$  subscripts denote quantities pertaining to the compound for which the ODP is desired. This equation has been altered slightly from the form given in the previous Assessment (Equation 1-6, WMO, 2003) because it was less clear how to account for compounds with both chlorine and bromine atoms using the previous form. For very short-lived substances (VSLs), the location and season of emission affect the amount of halogen that can make it to the stratosphere, making Equation (8-2) an inappropriate choice for ODP estimates of these gases (see Chapter 2 of this Assessment, as well as Chapter 2 of WMO, 2003).

### 8.2.2.1 ATMOSPHERIC LIFETIMES

The lifetimes of atmospheric trace gases given in Tables 8-1 and 8-2 have been assessed in Chapter 1. A detailed explanation of global lifetimes can be found in WMO (2003). For these reported lifetimes, it is assumed that the gases are uniformly mixed throughout the troposphere. This assumption is less accurate for gases with lifetimes  $< 1/2$  year, and is but one reason why single values for global lifetimes, ODPs, or GWPs are less appropriate for such short-lived gases (see Chapter 2). However, the majority of ozone-depleting substances and their replacements have atmospheric lifetimes greater than 2 years, much longer than tropospheric mixing times; hence their lifetimes, ODPs, and GWPs are not significantly altered by the location of sources within the troposphere.

### 8.2.2.2 FRACTIONAL RELEASE FACTORS

The distributions of species in the stratosphere depend on the competition between local photochemical removal processes and transport processes that carry the material from the entry point (mainly at the tropical tropopause) through, and out of, the stratosphere. Once a halogen source gas is in the stratosphere, release of a halogen atom from the source gas can occur through photolysis or chemical reaction. As already described in previous WMO reports (WMO, 2003), the fraction,  $f_i$ , of halocarbon  $i$  converted to an inorganic form by some time at a given location in the stratosphere can be given by:

$$f_i(x, y, z, t) = \frac{\rho_{i,entry} - \rho_i(x, y, z, t)}{\rho_{i,entry}} \quad (8-3)$$

where  $\rho_i(x, y, z, t)$  denotes the mixing ratio of the halocarbon at a given stratospheric location  $(x, y, z)$  at time  $t$ , and  $\rho_{i,entry}$  is the mixing ratio of species  $i$  in the air parcel when it entered the stratosphere. The value of  $\rho_{i,entry}$  can be estimated from knowledge of the age (time since entering the stratosphere) of the parcel at location  $(x, y, z)$  and the tropospheric time series of species  $i$ . With Equation (8-3), measurements of the halocarbon distributions within the stratosphere then can be used to define  $f_i(x, y, z, t)$ . The relative fractional release term used in Equation (8-2) is the ratio  $f_i / f_{CFC-11}$ , which is a measure of the local fractional release of inorganic halogen compounds relative to the fractional release of CFC-11. Conceptually, the fractional release factor should be globally integrated. In practice, a more limited range of measured correlations representing mid- to high latitudes, where ozone is highly sensitive to changes in the local photochemical removal rate, is generally used (e.g., Schauffler et al., 2003). The fractional release factors used in this report are given in Table 8-1. Except for the value for CFC-114, which is taken from Schauffler et al. (2003), all values are taken from WMO (2003). Most of these values have been derived from stratospheric observations, with models used to estimate the fractional release factors for a few source gases (Solomon et al., 1992; WMO, 2003).

The fractional release factors for hydrochlorofluorocarbons HCFC-141b and HCFC-142b included in Table 8-1 and used in the previous Assessment differ from the values derived by Schauffler et al. (2003) from stratospheric observations. These observations suggest values smaller by a factor of 3.1 and 4.5 for HCFC-141b and HCFC-142b, respectively. Because of the large growth rates of these compounds at the time the measurements were made and the resulting sensitivity of the fractional release values to age-of-air estimates, the authors of the

**Table 8-1. Lifetimes, relative fractional halogen release factors, and Ozone Depletion Potentials for halocarbons.** ODPs recommended in this Assessment and ODPs adopted in the Montreal Protocol are included.

Halocarbon *	Lifetime (years)	Relative Fractional Release Factor <sup>1</sup>	Semi-Empirical ODP	ODP in Montreal Protocol
<b>Annex A-I</b>				
CFC-11	45	1	1.0	1.0
CFC-12	100	0.60	1.0	1.0
CFC-113	85	0.75	1.0	0.8
CFC-114	300	0.28 ± 0.02 <sup>2</sup>	1.0	1.0
CFC-115	1700		0.44 <sup>†</sup>	0.6
<b>Annex A-II</b>				
Halon-1301	65	0.62	16	10.0
Halon-1211	16	1.18	7.1 <sup>3</sup>	3.0
Halon-2402	20	1.22	11.5	6.0
<b>Annex B-II</b>				
Carbon tetrachloride	26	1.06	0.73	1.1
<b>Annex B-III</b>				
Methyl chloroform	5.0	1.08	0.12	0.1
<b>Annex C-I</b>				
HCFC-22	12.0	0.35	0.05	0.055
HCFC-123	1.3	1.11	0.02	0.02
HCFC-124	5.8	0.52	0.02	0.022
HCFC-141b	9.3	0.72	0.12	0.11
HCFC-142b	17.9	0.36	0.07	0.065
HCFC-225ca	1.9	1.1	0.02	0.025
HCFC-225cb	5.8	0.5	0.03	0.033
<b>Annex E</b>				
Methyl bromide	0.7	1.12	0.51	0.6
<b>Others</b>				
Halon-1202	2.9		1.7 <sup>4</sup>	
Methyl iodide	see Chapter 2		see Chapter 2	
Methyl chloride	1.0	0.80	0.02	

\* Chemical formulae for the halocarbons are listed in Table 8-2 and also in Appendix C of this Assessment.

<sup>†</sup> Model-derived value, WMO (2003).

<sup>1</sup> From WMO (2003), Table 1-4, except for the value for CFC-114. For the EESC calculations in Section 1.8 of WMO (2003), slightly different relative fractional release factors were used by mistake for the halons. The values given here are used for the calculations presented in this Assessment.

<sup>2</sup> From Schauffler et al. (2003).

<sup>3</sup> The ODP of halon-1211 should have been reported as 5.3 in the previous Assessment (WMO, 2003), but was incorrectly reported as 6.0 due to a calculation error.

<sup>4</sup> WMO (2003), with adjustment for updated  $\alpha$  value.

previous Assessment did not adopt these new values. With no additional estimates available since this disagreement was discussed in the previous Assessment, the discrepancy remains an unresolved issue and we continue to use the older, model-derived values. Model estimates for all other gases agree with the values estimated from observations to within 2 times the quoted error bars of the observational estimates (Schauffler et al., 2003) except for

HCFC-22. The HCFC-22 value based on observations is about 17% lower than calculated in Solomon et al. (1992).

### 8.2.2.3 OZONE DESTRUCTION EFFECTIVENESS

Although the relative effectiveness of bromine compared with chlorine for ozone depletion, referred to as  $\alpha$ , is treated as a single, fixed quantity in Equation 8-

## HALOCARBON SCENARIOS, ODPs, AND GWPs

2 and in the calculation of EESC elsewhere in this Assessment Report, it represents a globally integrated result with sensitivity to many factors, including the kinetic parameters for chlorine and bromine species, the amount of inorganic bromine and inorganic chlorine in the background atmosphere, and atmospheric transport. The value of  $\alpha$  was assumed to be 45 in the previous Assessment, based partly on the results from Daniel et al. (1999) and Ko et al. (1998).

The value of  $\alpha$  has been recalculated for this Assessment with the Atmospheric Environmental Research, Inc. (AER), the Leeds-Bremen, and the University of Illinois two-dimensional models, which are discussed in Chapters 2 and 6. Using Jet Propulsion Laboratory (JPL) JPL-05 kinetics (preliminary version of Sander et al., 2006), the AER (D. Weisenstein, private communication) and Leeds-Bremen (B.-M. Sinnhuber, private communication) models calculate global values of 61 and 71, respectively. The University of Illinois (D. Wuebbles, private communication) model suggests a value of 57 using JPL-02 kinetics (Sander et al., 2002). The change in kinetics recommendations from 1997 are thought to play a relatively minor role in the increased estimates of the  $\alpha$  value. The Leeds-Bremen model, when using JPL-97 rates (DeMore et al., 1997), calculates a reduced  $\alpha$  value of 64 compared with the 71 with the JPL-05 kinetics. The AER model value is also higher than its previously calculated value when using JPL-97 rates; however, changes have been made in the model in addition to kinetic rates that also could have affected the  $\alpha$  value. The AER value would have been 52 with the JPL-97 rates if a methyl bromide ( $\text{CH}_3\text{Br}$ ) stratosphere fractional release value of 1.12 relative to CFC-11 was applied to the results of Ko et al. (1998); however, the calculated release value from the current AER model is larger than 1.12, perhaps implying a value for  $\alpha$  lower than 52 (M. Ko, private communication). Thus, there is no simple way to be certain of the precise AER  $\alpha$  value with JPL-97 kinetics.

The reasons for the variations in the calculated  $\alpha$  values from these models apparently arise not from kinetics changes alone, but also from differences in other model processes, such as transport, the ozone loss spatial distribution, etc. The differences have not yet been explained in the literature. Nevertheless, due to the consistently larger values recently calculated with these well-documented models compared with the previously assumed value of 45, and because the Leeds-Bremen model suggests an even higher value when additional stratospheric bromine is considered to account for VSLs (a value of 73 for an additional 6 ppt of stratospheric bromine), we now recommend an  $\alpha$  value of 60 for global ozone destruction. However, we emphasize the relatively

large model-dependent range of values discussed in the previous paragraph.

In Section 8.3, a value of 65 is used for  $\alpha$  when simulating Antarctic conditions, based on the results of Chipperfield and Pyle (1998) for Arctic conditions. These calculations assumed DeMore et al. (1994) kinetic rates; a calculation using updated rates is not currently available.

For fluorine, the relative effectiveness compared with chlorine for ozone destruction is negligibly small based on the results from Ravishankara et al. (1994) and Wallington et al. (1995).

### 8.2.2.4 ODP VALUES

The most significant change in ODPs since the previous Assessment is for the bromocarbons, due to the increase in the recommended value of  $\alpha$  from 45 to 60. This  $\alpha$  increase leads directly to an increase in the semi-empirical ODPs of all bromocarbons of 33%. The ODP of halon-1211 was also incorrectly reported in the previous Assessment to be 6.0 due to a calculation error; it should have been reported as 5.3. The ODPs of the chlorocarbons remain the same as those reported in WMO (2003), except for CFC-114. In WMO (2003), the ODP for CFC-114 was derived from a model; because the fractional chlorine release and lifetime are available, the semi-empirical ODP is reported here. Although the recommended value of the methyl chloride ( $\text{CH}_3\text{Cl}$ ) lifetime has been decreased from 1.3 to 1.0 (Chapter 1), the ODP remains unchanged to the reported precision.

### 8.2.3 Direct Global Warming Potentials

Halocarbons absorb terrestrial radiation (long wavelength infrared radiation emitted from the Earth's surface) and contribute to the radiative forcing of the climate system. They generally have strong absorption features in the atmospheric window region (at approximately 8-12 micrometers) where there is little absorption by atmospheric gases. This absorption reduces the amount of outgoing energy from the Earth-atmosphere system and leads to a direct radiative forcing. It is this forcing that plays an important role in the calculations of the direct GWPs discussed in this section.

The change in net radiation at the tropopause caused by a given change in greenhouse gas concentration or mass is referred to as radiative efficiency. Radiative efficiency has units of  $\text{W m}^{-2} \text{ppb}^{-1}$  or  $\text{W m}^{-2} \text{kg}^{-1}$ ; it is calculated using radiative transfer models of the atmosphere and depends upon the strength and spectral position of a compound's absorption bands. The Absolute Global Warming Potential (AGWP) has units of  $\text{W m}^{-2} \text{ppb}^{-1} \text{yr}$  or  $\text{W m}^{-2} \text{k}^{-1} \text{yr}$  and quantifies the future integrated radiative forcing of a unit

mass pulse emission of a greenhouse gas; it can be defined as:

$$AGWP_x(t') = \int_0^{t'} F_x [x(t)] dt \quad (8-4)$$

where  $F_x$  is the radiative forcing per unit mass of species  $x$ ,  $x(t)$  describes the decay with time of a unit pulse of compound  $x$ , and  $t'$  is the time horizon considered. To compare the relative integrated effects of various compounds on climate, the Global Warming Potential concept was developed. The Global Warming Potential (IPCC, 1990; 2001) can be defined as:

$$GWP_x(t') = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right) dt}{\int_0^{t'} F_{CO_2} R(t) dt} \quad (8-5)$$

where  $F_{CO_2}$  is the radiative forcing of carbon dioxide ( $CO_2$ ),  $R(t)$  is the response function that describes the decay of an instantaneous pulse of  $CO_2$ , and the decay of the pulse of compound  $x$  has been rewritten assuming it obeys a simple exponential decay curve determined by a response time of  $\tau_x$ . Both  $F_x$  and  $F_{CO_2}$  are generally given in units of  $W m^{-2} kg^{-1}$ . The unit pulse response terms lead to a dependence of GWPs on the integration time horizon; compounds that decay more quickly (slowly) than the reference ( $CO_2$ ) have GWPs which decrease (increase) with increasing time horizon. As shown in Equations (8-4) and (8-5), the most common definition of GWPs applies to pulsed emissions. However, indices have also been developed to evaluate the effect of sustained emissions (Berntsen et al., 2005; Johnson and Derwent, 1996; Shine et al., 2005a).

The GWP index has three major advantages over other indices used to measure the contribution of halocarbons to global warming: transparency, simplicity, and widespread acceptance. Disadvantages of the GWP index include: (1) GWPs compare contributions with radiative forcing and not with the often more relevant factors of temperature change or economic damage; (2) impacts at different times in the future are given equal weight (for times between the time of the pulse and the time of the pulse plus the time horizon) (Fuglestad et al., 2000, 2003; Manne and Richels, 2001; O'Neill, 2000; Shine et al., 2005a; Smith and Wigley, 2000a, b; Wigley, 1998); and (3) GWPs are dependent on assumptions regarding other gas concentrations due to spectral overlaps of absorption bands (e.g., Hurley et al., 2005)). Various alternatives

have been presented to overcome some of these limitations, but discussions of these are beyond the scope of this chapter.

Direct GWPs are tabulated in Table 8-2. With the recent publication of the IPCC/TEAP (2005) Special Report and the soon to be released IPCC Fourth Assessment Report, we will limit additional discussion of GWPs to updates since the last Ozone Assessment. There are four reasons that updates have been made: (1) a change in  $F_{CO_2}$  due to an increase in the  $CO_2$  atmospheric mixing ratio from 370 parts per million (ppm) to 378 ppm; (2) a new  $CO_2$  response function; (3) updates to two atmospheric lifetimes; and (4) new radiative forcing recommendations.

The change in  $CO_2$  mixing ratio reflects the continuing increase in the atmospheric concentration of this radiatively important gas. This increased atmospheric abundance of  $CO_2$  results in a lower radiative efficiency due to the  $CO_2$  bands becoming slightly more saturated. The formula used to calculate the forcing has also been changed to

$$5.35 \ln\left(\frac{c_0 + \Delta c}{c_0}\right) \quad (8-6)$$

where  $c_0$  is 378 ppm and  $\Delta c$  is the added pulse. This formula is adopted because it is more consistent with current estimates of the radiative forcing associated with a doubling of  $CO_2$  (IPCC, 2001). The mixing ratio used in Equation (8-6) in conjunction with a pulse of 1 ppm leads to a  $CO_2$  radiative efficiency of  $0.0141 W m^{-2} ppm^{-1}$  compared with a value of  $0.0153 W m^{-2} ppm^{-1}$  from the previous Assessment. A new pulse response function for  $CO_2$  was calculated with the Bern25CC model (Joos et al., 2001; Plattner et al., 2001) for a constant  $CO_2$  background mixing ratio of 378 ppm and a pulse size of 40 GtC. The combination of this slightly changed response function and the smaller radiative forcing leads to  $CO_2$  AGWPs of 0.192, 0.676, and 2.223  $W m^{-2} ppm^{-1} yr$  for time horizons of 20, 100, and 500 years, respectively (F. Joos, personal communication). These AGWPs are smaller than those of IPCC (2001) by 7.2%, 2.9%, and 0.8% for these same respective time horizons. GWPs are calculated relative to  $CO_2$  so these lower  $CO_2$  AGWPs result in increased GWP values by these same percentages in the absence of other changes.

Lifetimes have been updated for trifluoromethylsulfurpentafluoride ( $SF_5CF_3$ ) and methyl chloride ( $CH_3Cl$ ). A discussion of these updates can be found in Chapter 1. We also recommend updated radiative efficiencies of six compounds compared with WMO (2003):

HALOCARBON SCENARIOS, ODPs, AND GWPs

Table 8-2. Direct Global Warming Potentials for selected gases.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency <sup>1</sup> (W m <sup>-2</sup> ppbv <sup>-1</sup> )	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Carbon dioxide	CO <sub>2</sub>	1.41 × 10 <sup>-5 2</sup>		1	1	1
Nitrous oxide	N <sub>2</sub> O	3.03 × 10 <sup>-3</sup>	114 <sup>3</sup>	289	298	153
<b>Chlorofluorocarbons</b>						
CFC-11	CCl <sub>3</sub> F	0.25	45	6,730	4,750	1,620
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	0.32	100	10,990	10,890	5,200
CFC-13	CCIF <sub>3</sub>	0.25	640	10,800	14,420	16,430
CFC-113	CCl <sub>2</sub> FCCIF <sub>2</sub>	0.30	85	6,540	6,130	2,690
CFC-114	CCIF <sub>2</sub> CCIF <sub>2</sub>	0.31	300	8,040	10,040	8,730
CFC-115	CCIF <sub>2</sub> CF <sub>3</sub>	0.18	1700	5,310	7,370	9,990
<b>Hydrochlorofluorocarbons</b>						
HCFC-21	CHCl <sub>2</sub> F	0.14	1.7	530	151	46
HCFC-22	CHClF <sub>2</sub>	0.20	12.0	5,160	1,810	549
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	0.14	1.3	273	77	24
HCFC-124	CHClFCF <sub>3</sub>	0.22	5.8	2,070	609	185
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	0.14	9.3	2,250	725	220
HCFC-142b	CH <sub>3</sub> CCIF <sub>2</sub>	0.20	17.9	5,490	2,310	705
HCFC-225ca	CHCl <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	0.20	1.9	429	122	37
HCFC-225cb	CHClFCF <sub>2</sub> CCIF <sub>2</sub>	0.32	5.8	2,030	595	181
<b>Hydrofluorocarbons</b>						
HFC-23	CHF <sub>3</sub>	0.19 <sup>4</sup>	270	11,990	14,760	12,230
HFC-32	CH <sub>2</sub> F <sub>2</sub>	0.11 <sup>4</sup>	4.9	2,330	675	205
HFC-41	CH <sub>3</sub> F	0.02	2.4	323	92	28
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	0.23	29	6,340	3,500	1,100
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	0.18	9.6	3,400	1,100	335
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	0.16 <sup>4</sup>	14.0	3,830	1,430	435
HFC-143	CH <sub>2</sub> FCHF <sub>2</sub>	0.13	3.5	1,240	353	107
HFC-143a	CH <sub>3</sub> CF <sub>3</sub>	0.13	52	5,890	4,470	1,590
HFC-152	CH <sub>2</sub> FCH <sub>2</sub> F	0.09	0.60	187	53	16
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	0.09	1.4	437	124	38
HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	0.26 <sup>4</sup>	34.2	5,310	3,220	1,040
HFC-236cb	CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>	0.23	13.6	3,630	1,340	407
HFC-236ea	CHF <sub>2</sub> CHFCF <sub>3</sub>	0.30	10.7	4,090	1,370	418
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	0.28	240	8,100	9,810	7,660
HFC-245ca	CH <sub>2</sub> FCF <sub>2</sub> CHF <sub>2</sub>	0.23	6.2	2,340	693	211
HFC-245fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	0.28	7.6	3,380	1,030	314
HFC-365mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	0.21	8.6	2,520	794	241
HFC-43-10mee	CF <sub>3</sub> CHFCHFCF <sub>2</sub> CF <sub>3</sub>	0.40	15.9	4,140	1,640	499
<b>Chlorocarbons</b>						
Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	0.06	5.0	506	146	45
Carbon tetrachloride	CCl <sub>4</sub>	0.13	26	2,700	1,400	435
Methyl chloride	CH <sub>3</sub> Cl	0.01	1.0	45	13	4

Table 8-2, continued.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency <sup>1</sup> (W m <sup>-2</sup> ppbv <sup>-1</sup> )	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
<b>Bromocarbons</b>						
Methyl bromide	CH <sub>3</sub> Br	0.01	0.7	17	5	1
Halon-1201	CHBrF <sub>2</sub>	0.14	5.8	1,380	404	123
Halon-1211	CBrClF <sub>2</sub>	0.30	16	4,750	1,890	574
Halon-1301	CBrF <sub>3</sub>	0.32	65	8,480	7,140	2,760
Halon-2402	CBrF <sub>2</sub> CBrF <sub>2</sub>	0.33	20	3,680	1,640	503
<b>Fully fluorinated species</b>						
Sulfur hexafluoride	SF <sub>6</sub>	0.52	3200	16,260	22,810	32,600
Trifluoromethylsulfur- pentafluoride	SF <sub>5</sub> CF <sub>3</sub>	0.57	650- 950	13,120- 13,180	17,540- 17,960	20,060- 22,360
Perfluoromethane	CF <sub>4</sub>	0.10 <sup>4</sup>	50000	5,210	7,390	11,190
Perfluoroethane	C <sub>2</sub> F <sub>6</sub>	0.26	10000	8,620	12,200	18,180
Perfluoropropane	C <sub>3</sub> F <sub>8</sub>	0.26	2600	6,310	8,830	12,450
Perfluorobutane	C <sub>4</sub> F <sub>10</sub>	0.33	2600	6,330	8,850	12,480
Perfluorocyclobutane	c-C <sub>4</sub> F <sub>8</sub>	0.32	3200	7,310	10,250	14,660
Perfluoropentane	C <sub>5</sub> F <sub>12</sub>	0.41	4100	6,510	9,150	13,260
Perfluorohexane	C <sub>6</sub> F <sub>14</sub>	0.49	3200	6,620	9,290	13,280
Perfluorodecalin	C <sub>10</sub> F <sub>18</sub>	0.56 <sup>5</sup>	1000	5,500	7,510	9,440
<b>Halogenated alcohols and ethers</b>						
HFE-125	CHF <sub>2</sub> OCF <sub>3</sub>	0.44	136	13,790	14,910	8,490
HFE-134	CHF <sub>2</sub> OCHF <sub>2</sub>	0.45	26	12,190	6,320	1,960
HFE-143a	CH <sub>3</sub> OCF <sub>3</sub>	0.27	4.3	2,630	756	230
HCFE-235da2	CHF <sub>2</sub> OCHClCF <sub>3</sub>	0.38	2.6	1,230	349	106
HFE-245fa2	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	0.31	4.9	2,280	659	200
HFE-254cb2	CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>	0.28	2.6	1,260	359	109
HFE-7100 (HFE-44-9)	CH <sub>3</sub> OC <sub>4</sub> F <sub>9</sub>	0.31	5.0	1,390	404	123
HFE-7200 (HFE-56-9)	C <sub>2</sub> H <sub>5</sub> OC <sub>4</sub> F <sub>9</sub>	0.30	0.77	200	57	17
HFE-245cb2	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>3</sub>	0.32	5.1	2,440	708	215
HFE-347mcc3	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	0.34	5.2	1,980	575	175
HFE-356pcc3	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	0.33	0.93	386	110	33
HFE-374pc2	CH <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>	0.25	5.0	1,930	557	169
	CH <sub>3</sub> OCF(CF <sub>3</sub> ) <sub>2</sub>	0.31	3.4	1,200	343	104
HFE-43-10pccc124 <sup>a</sup>	CHF <sub>2</sub> OCF <sub>2</sub> OC <sub>2</sub> F <sub>4</sub> OCHF <sub>2</sub>	1.37	6.3	6,320	1,870	569
	(CF <sub>3</sub> ) <sub>2</sub> CHOH	0.28	2.0	764	217	66
HFE-236ca12	CHF <sub>2</sub> OCF <sub>2</sub> OCHF <sub>2</sub>	0.66	12.1	8,040	2,820	859
HFE-338pcc13	CHF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>	0.87	6.2	5,070	1,500	456
<b>Species whose lifetimes have a high uncertainty</b>						
Nitrogen trifluoride	NF <sub>3</sub>	0.21 <sup>4</sup>	740	13,370	18,000	21,270
Perfluorocyclopropane	c-C <sub>3</sub> F <sub>6</sub>	0.42	>1000	>12,700	>17,340	>21,800
HFE-227ea	CF <sub>3</sub> CHFOCF <sub>3</sub>	0.40	11	4,540	1,540	468
HFE-236ea2	CHF <sub>2</sub> OCHF <sub>2</sub> CF <sub>3</sub>	0.44	5.8	3,370	989	301
HFE-236fa	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>3</sub>	0.34	3.7	1,710	487	148
HFE-245fa1	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>3</sub>	0.30	2.2	1,010	286	87

## HALOCARBON SCENARIOS, ODPs, AND GWPs

**Table 8-2, continued.**

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency <sup>1</sup> (W m <sup>-2</sup> ppbv <sup>-1</sup> )	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
HFE-329mcc2	CHF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	0.49	6.8	3,060	919	279
HFE-338mcf2	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	0.43	4.3	1,920	552	168
HFE-347mcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	0.41	2.8	1,310	374	114
HFE-356mec3	CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub> CF <sub>3</sub>	0.30	0.94	355	101	31
HFE-356pcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>	0.37	2.0	931	265	80
HFE-356pcf3	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	0.39	3.6	1,760	502	153
	CHF <sub>2</sub> OCH(CF <sub>3</sub> ) <sub>2</sub>	0.41	3.1	1,330	379	115
	-(CF <sub>2</sub> ) <sub>4</sub> CH(OH)-	0.30	0.85	254	72	22

Note: Values are calculated for a CO<sub>2</sub> mixing ratio of 378 ppm, compared with 370 ppm in IPCC/TEAP (2005) and WMO (2003); this leads to slightly smaller CO<sub>2</sub> AGWPs.

<sup>a</sup> Referred to as H-Galden 1040x in previous Assessments.

<sup>1</sup> All values from IPCC/TEAP (2005) unless otherwise noted.

<sup>2</sup> See Section 8.2.3.

<sup>3</sup> This value is an adjustment time that includes feedbacks of emissions on the lifetime.

<sup>4</sup> See Table 8-3.

<sup>5</sup> From Shine et al. (2005b).

the hydrofluorocarbons HFC-134a (CFH<sub>2</sub>CF<sub>3</sub>), HFC-23 (CHF<sub>3</sub>), HFC-32 (CH<sub>2</sub>F<sub>2</sub>), HFC-227ea (CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub>), and CF<sub>4</sub> and NF<sub>3</sub>. The radiative efficiency values used in the previous Assessment, the currently recommended values, and the values presented in the pertinent references are presented in Table 8-3.

Since the last Assessment (WMO, 2003), the radiative efficiency of HFC-134a has been studied by Forster et al. (2005). Various laboratory cross sections and radiative transfer models were used to assess the primary sensitivities of the radiative efficiency. The integrated absorption cross sections from six independent laboratory studies of the bands most significant to the radiative efficiency calculation differed by less

than 5%. While the models showed some difference in the cloudy-sky forcing for a single atmospheric profile, the best estimates of the radiative efficiency converged to a value of 0.16 W m<sup>-2</sup> ppbv<sup>-1</sup>. This value is adopted; it is close to that used in the previous Assessment (0.15 W m<sup>-2</sup> ppbv<sup>-1</sup>) (WMO, 2003).

The radiative efficiency of CF<sub>4</sub> has been studied by Hurley et al. (2005) since the previous ozone Assessment. There is good agreement (within 4%) in the absorption cross sections measured in two independent laboratory studies reported by Hurley et al. (2005) and in the study of Nemtchinov and Varanasi (2003). The radiative efficiency reported by Hurley et al. (2005), 0.102 W m<sup>-2</sup> ppbv<sup>-1</sup>, is 15% greater than calculated by Myhre et al. (1998).

**Table 8-3. Radiative efficiency estimates for six compounds whose recommended values have changed since the previous Assessment.** All values are in units of W m<sup>-2</sup> ppbv<sup>-1</sup>.

Species	WMO (2003)	Hurley et al. (2005)	Forster et al. (2005)	Jain et al. (2000)	Sihra et al. (2001)	Gohar et al. (2004)	This Assessment
HFC-134a	0.15		0.16	0.20	0.159	0.155-0.166	0.16
CF <sub>4</sub>	0.08	0.102		0.089 <sup>1</sup>	0.116		0.10
HFC-23	0.16			0.248	0.171	0.181-0.193	0.19
HFC-32	0.09			0.155	0.105	0.110-0.111	0.11
HFC-227ea	0.30			0.322	0.256	0.243-0.271	0.26
NF <sub>3</sub>	0.13						0.21 <sup>2</sup>

<sup>1</sup> For a constant vertical mixing ratio profile.

<sup>2</sup> From Robson et al. (2006).

About a 10% increase is explained by the larger cross section and the remaining 5% is believed to be due to differing radiative transfer codes employed.

Since the last ozone Assessment, radiative efficiencies of HFC-23, HFC-32, and HFC-227ea have been studied by Gohar et al. (2004), using two independent sets of radiation codes. There is a greater than 20% difference in the calculated radiative efficiencies of these gases reported by Sihra et al. (2001) and Jain et al. (2000), both of which were considered in the previous Assessment. At the time of the previous Assessment, the reason for the differences was not clear and averages of the two datasets were used. While the reason for the differences between the Jain et al. and Sihra et al. values are still unknown, the results of Gohar et al. (2004) support the values given by Sihra et al. (2001), leading to an update of the recommendations given in Table 8-3. The calculations by Gohar et al. (2004) also illustrate the sensitivity of the radiative efficiency calculations to the particular model choice.

The radiative efficiency of  $\text{NF}_3$  has been re-evaluated recently by Robson et al. (2006). The radiative efficiency used in previous Assessments (IPCC, 2001; WMO, 1999, 2003) was calculated from the absorption cross section data of Molina et al. (1995) by K.P. Shine using the simple radiative method given in Pinnock et al. (1995), as no radiative efficiency was provided in the Molina et al. (1995) work. The Robson et al. (2006) study suggests that the more intense infrared (IR) features reported by Molina et al. (1995) were saturated, causing the inferred radiative efficiency to be too small. Molina et al. (1995) did not report the precise conditions used to derive their absorption cross section values, making an unambiguous evaluation of the importance of saturation impossible. We adopt the radiative efficiency of  $0.21 \text{ W m}^{-2} \text{ ppb}^{-1}$  from the more comprehensive study by Robson et al. (2006).

The  $2\sigma$  uncertainty associated with the direct GWPs shown is estimated to be  $\pm 35\%$ . This value has been adopted from previous ozone and climate Assessments (IPCC, 2001; WMO, 2003; IPCC/TEAP, 2005) and is primarily due to uncertainties in the radiative efficiencies and lifetimes of the halocarbons and to uncertainties in our understanding of the carbon cycle (IPCC, 2001). However, because the uncertainties in the carbon cycle are thought to be an important part of this uncertainty, the error in the relative GWP values among halocarbons should be less than 35% (IPCC, 2001).

The indirect radiative forcing and indirect GWPs of a species quantify the radiative effects from changes in abundances of other greenhouse gases resulting from the

addition of the species considered. Because the indirect forcing and GWPs due to stratospheric ozone loss depend on the future evolution of stratospheric ozone and thus on the specific ODS emission scenario, these are presented in Section 8.5 of this chapter, after the halocarbon scenarios are discussed.

## 8.2.4 Degradation Products and Their Implications for ODPs and GWPs

Degradation products of CFCs, HCFCs, and HFCs have been discussed in IPCC/TEAP (2005). The main conclusion was that the intermediate degradation products of most long-lived CFCs, HCFCs, and HFCs have shorter lifetimes than the source gases, and therefore have lower atmospheric concentrations and smaller radiative forcings. Intermediate products and final products are removed from the atmosphere via deposition and washout processes and may accumulate in oceans, lakes, and other aquatic reservoirs. Trifluoroacetic acid is a persistent degradation product of some HCFCs and HFCs and is removed from the atmosphere mainly by wet deposition. Its sources (natural and anthropogenic), sinks, and potential environmental effects have been reviewed by Tang et al. (1998), Solomon et al. (2003), and IPCC/TEAP (2005). The available environmental risk assessment and monitoring data indicate that the source of trifluoroacetic acid from the degradation of HCFCs and HFCs will not result in environmental concentrations capable of significant ecosystem damage.

## 8.3 FUTURE HALOCARBON SOURCE GAS CONCENTRATIONS

### 8.3.1 Introduction

Projections of future atmospheric halocarbon mixing ratios require knowledge of future emissions and atmospheric/oceanic loss rates in addition to current atmospheric abundances. In this section, we use estimates of these quantities in a simple box model to calculate average future surface mixing ratios, which are assumed to be related to mean atmospheric mixing ratios by a fixed factor. These calculated mixing ratios are used to generate equivalent effective stratospheric chlorine (EESC) estimates, which are used to evaluate the effects of different halocarbon production/emission scenarios and hypothetical test cases. The lifetimes presented in Table 8-1 (see also Chapter 1) are estimated from the loss rates of the ODSs and are used in the box model. Any future changes in the hydroxyl radical (OH) amount (IPCC, 2001) and/or

## HALOCARBON SCENARIOS, ODPs, AND GWPs

distribution, and any changes in circulation (see, e.g., Chapters 5 and 6) that might affect lifetimes, are neglected. To include more complicated atmospheric interactions such as these, more sophisticated two-dimensional (2-D) and three-dimensional (3-D) atmospheric models should be used.

The box model approach used here has also been used in previous Assessments (WMO, 1995; 1999; 2003). Global mean mixing ratios are calculated using the equation

$$\frac{d\rho_i}{dt} = F_i E_i - \frac{\rho_i}{\tau_i} \quad (8-7)$$

where  $\rho$  is the global mean mixing ratio (in ppt),  $\tau$  is the total atmospheric lifetime,  $E$  is the emission rate (in kg/year), and  $F$  is the factor that relates the mass emitted to the global mean mixing ratio, given by

$$F_i = \frac{5.68 \times 10^{-9}}{M_i} \quad (8-8)$$

where  $F$  is in units of ppt/kg, and  $M$  is the molecular weight (in kg/mole). The  $i$  subscripts refer to the species considered in the calculation. As in the previous ozone Assessment, the calculated global mean mixing ratios are multiplied by a factor of 1.07 to represent surface mixing ratios. This factor is meant to account for the general decrease of the halocarbon mixing ratios with altitude above the tropopause. Using a constant factor such as this neglects the dependence of this factor on the particular species and neglects any change in this factor that could be caused by changes in circulation or by the variability of the surface emission (and the resulting variability in the atmospheric vertical distribution).

Accurate projections of emissions require an understanding of the amount of halocarbons in equipment and product banks, the rates of release from these banks, the quantity of equipment and products using ODSs that will be put into service, emissive uses, and the future production of ODSs. Banks here are defined as the quantity of ODSs produced but not yet emitted to the atmosphere. Due to the importance of policy decisions, energy cost, technological advancement, and economic growth rates in estimating future production and banks, the uncertainty level in future emissions remains high. However, with each passing year, as more years of emissions can be calculated from atmospheric abundance observations and fewer years remain for the legal consumption of ODSs under the Montreal Protocol, future projections should become more constrained.

Scenarios and test cases have been developed to describe the possible range of future atmospheric abundances of ODSs. These cases are generated using the current understanding of global production, emission, and banks of the most widely used halocarbons. Scenario A1 is meant to represent the current baseline or “best guess” scenario, analogous to the Ab scenario from the previous Assessment. An estimated “maximum” scenario, developed for previous Assessments, is not generated for this Assessment because developed and developing countries have produced less CFCs in 2000-2004 than allowed under the Montreal Protocol and the HCFC production in developing countries is not controlled before 2016. Hence, any attempt to develop such a scenario would be largely speculative on our part. Indeed, it is this uncertainty in future HCFC emission that represents a major reason for the difference that will be discussed later between the current A1 scenario and the comparable Ab scenario of the previous Assessment.

Consistent with past Assessments, our approach to relating annual production, emission, and banks sizes places most confidence on the emission values calculated from atmospheric observations and global lifetimes. Accurate estimates of yearly averaged ODS emissions from atmospheric observations are possible when global lifetimes are long and accurately known, and accurate global mixing ratio observations of ODSs are available. This approach, when used to estimate current bank sizes from historic production and emission data, is sometimes referred to as a top-down approach. In past Assessments, any inconsistency between mixing ratio observations and emission estimates based on the best knowledge of ODS production, sales, and application-specific release functions was eliminated by adjusting the bank size so the emissions would be consistent with the observations. The bank that remained after the sum of adjustments for all years was used in the future projections. Because the bank is an accumulating difference often between two large numbers, this method has an uncertainty that is difficult to quantify and can lead to unreasonable bank sizes; indeed the estimate of no bank in 2002 for CFC-12 in the previous ozone Assessment is such an example (IPCC/TEAP, 2005). One way an unreasonable bank could be attained is in a case in which annual production numbers are accurately known, but the atmospheric lifetime assumed is incorrect. In such a case, a lifetime that is too small (large) will result in an annual release from the bank that must be too large (small) for calculated mixing ratios to agree with observations. Such a situation would occur year after year and could result in a potentially significant error in the bank estimate today, depending on the compound (Daniel et al.,

2006). But without an independent estimate of bank size, such an error would be difficult to identify.

A different approach for determining bank sizes is taken in this Assessment because of the new independent estimates of bank sizes for several ODSs for the years 2002 and 2015 (Clodic and Palandre, 2004; IPCC/TEAP, 2005). These estimates are independent of atmospheric abundance observations and have been determined from the number of units of equipment that use a particular ODS and the amount of ODS in each unit. This is commonly referred to as a bottom-up approach. An extensive explanation of this methodology can be found in IPCC/TEAP (2005). Future emissions until 2015 estimated in this Assessment are calculated by beginning with the 2002 bottom-up bank from IPCC/TEAP (2005), and then by adding annual production and applying a constant annual bank emission factor needed to attain the bottom-up bank estimated in 2015 by IPCC/TEAP (2005). After 2015, emissions are calculated using the same constant bank emission factors as immediately before 2015. Thus, when bottom-up bank size estimates for 2002 and 2015 are available for a particular ODS, the scenarios in this chapter are consistent with them in most cases.

Bottom-up estimates are also not without problems; indeed bottom-up 2002 emission estimates for CFC-11, HCFC-141b, and HCFC-142b (IPCC/TEAP, 2005), which are dominated by emissions from foams, are smaller by more than a factor of two when compared with what is needed to be consistent with mixing ratio observations. Nevertheless, it is felt that these bottom-up bank estimates represent an important new constraint to current bank sizes that warrants a large role in the future projections in this chapter. In Sections 8.3.2.1 and 8.3.4, more discussion of the uncertainties involved with bottom-up and top-down emission estimates and their potential effects on the scenarios is presented.

### 8.3.2 Baseline Scenario (A1)

In this chapter, estimates of future banks and emissions have been calculated for most ODSs using annual production reported to the United Nations Environment Programme (UNEP, 2005), emissions estimated from atmospheric observations, and bank size estimates based on the bottom-up calculations of IPCC/TEAP (2005). The specific information used for each ODS considered is described in Table 8-4. Due to the uncertainty in the importance of and likely future trends in very short-lived ( $\tau < \sim 0.5$  years) organic bromine and chlorine source gases, they are not considered in any of these scenarios. However, the bromocarbons considered in this chapter cannot explain the entire stratospheric inorganic bromine

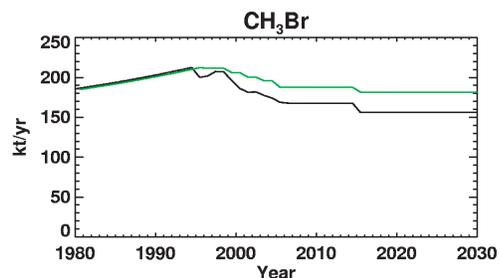
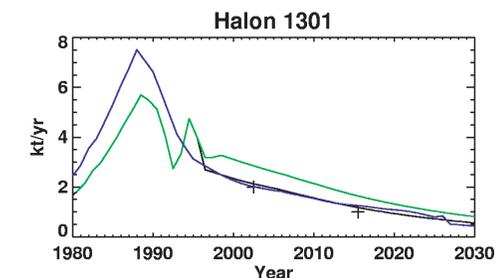
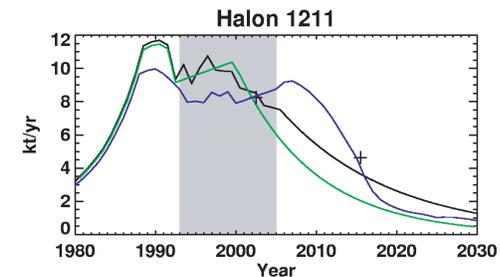
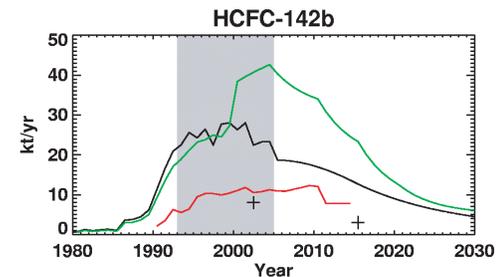
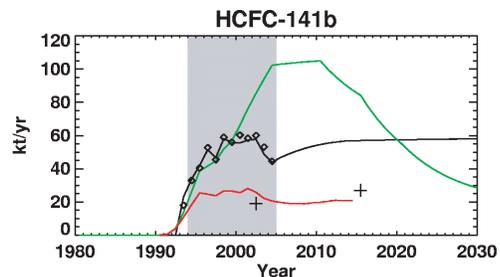
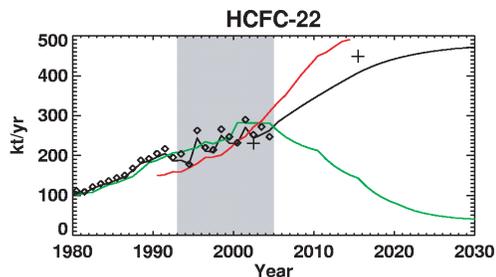
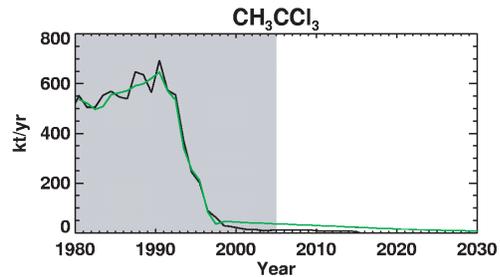
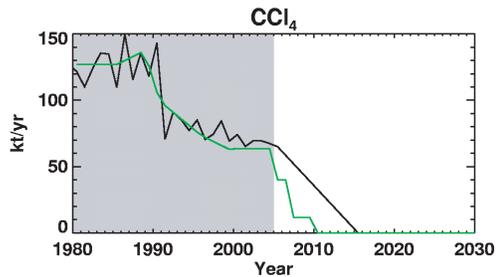
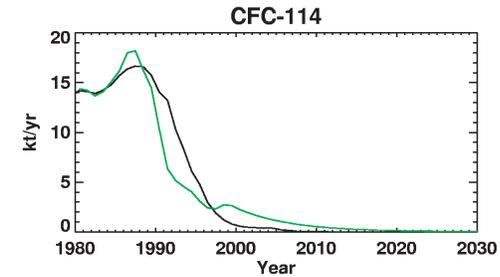
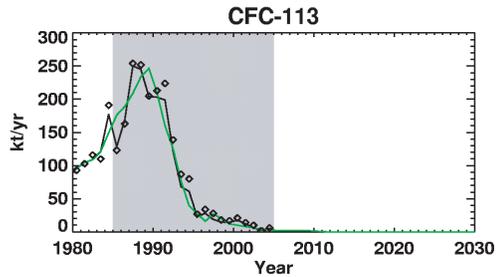
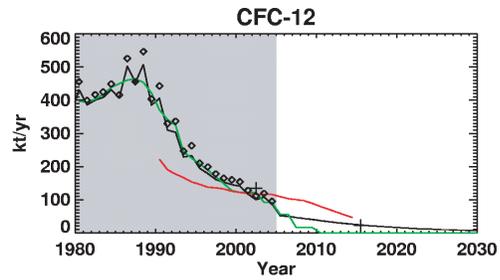
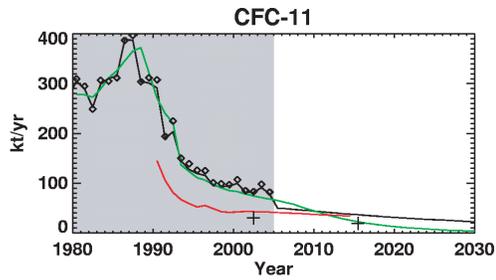
abundance alone, so the very short-lived gases may prove to be important. Detailed information about these compounds can be found in Chapter 2.

It should be noted that the assumptions made in calculating the baseline scenario are critical to the interpretation of the reduced production and emission scenarios based on it. For example, if the production and/or bank sizes and/or future production rates are underestimated in the baseline scenario, the “no emission/production” results presented in the scenarios would be underestimates of the potential reduction benefit.

#### 8.3.2.1 EMISSIONS

In Figure 8-1, the emission estimates from the 1-box model for the baseline scenario, A1, are compared with those of the Ab “best guess” scenario from the previous Assessment, with the IPCC/TEAP (2005) (business-as-usual (BAU) scenario) emissions, with the emissions of Clodic and Palandre (2004), and with the emissions calculated using the 12-box model discussed in Chapter 1. The emissions calculated with the 1-box model are calculated directly from mixing ratio observations (those shaded in Table 8-5) as are the emissions calculated with the 12-box model. The 12-box model, by having some vertical resolution, includes some changes in atmospheric lifetimes due to variations in atmospheric abundance distributions caused by increasing or decreasing trends; hence, the 12-box model can presumably better determine the relationship between surface mixing ratios and global averages and can better estimate changes in global lifetimes that arise from different atmospheric distributions. The comparisons between the A1 estimated emissions (1-box model) and the 12-box emissions are good most times, but do show some systematic differences. Throughout the measurement periods (shaded regions in the figure), the 12-box model consistently estimates more emission than the 1-box model, with the cumulative differences ranging from a 1.2% higher emission for HCFC-141b through the measurement period as calculated by the 12-box model, to a 6.3% higher emission for CFC-12. There are also noticeable differences between A1 and Ab emissions, many of which are due to the additional information acquired from continued measurements over the past 4 years. Important differences between A1 and Ab include the larger future emissions of CFC-11 and CFC-12, due to their larger estimated banks in A1. The CFC-11 increase in emission past 2010 is also due to a decrease of the bank release rate from plastic foams. The CFC-11 and CFC-12 bank size differences as calculated by the bottom-up method (IPCC/TEAP, 2005) and the top-down method of WMO (2003) have been shown by Daniel et al. (2006) to be large

# HALOCARBON SCENARIOS, ODPs, AND GWPs



**Figure 8-1.** Comparison of scenario A1 emissions (black) with those of scenario Ab of the previous Assessment (green), the emissions of Clodic and Palandre (2004) (red), the IPCC/TEAP (2005) emissions (crosses), and emissions calculated from atmospheric abundance observations using a 12-box model (small diamonds), all in units of kilotons per year. Corrected data are used for emissions of halon-1211 according to TEAP (2005) and hence differ from the data reported in IPCC/TEAP (2005). Also shown for halon-1301 are the emissions estimates from the 2002 report of the Halons Technical Options Committee (HTOC) (UNEP, 2003) and, for halon-1211, updates to that report (blue curves). Shaded regions indicate years for which A1 emissions are determined with a 1-box model (see text) so that calculated mixing ratios are exactly equal to the observations. At times, the emissions from the two Assessments are identical, causing the green curve to obscure the black one.

**Table 8-4. Assumptions made in obtaining production and emission estimates for the baseline A1 scenario.**

---

**General Approach for All Species**

---

**Production:** For the years when production is reported to UNEP, reported values (or best estimates of production values for cases in which reporting is incomplete or reporting is made by classes of compounds) are used. Before this, WMO (2003) production values are generally used. In the future, annual figures are determined from the lesser of the Montreal Protocol limitations and the most recent annual estimates.

**Emission:** For the years when abundance observations are available, emissions are calculated using the box model described in Section 8.3.1 with the lifetimes of Table 8-1. Emissions before this are usually consistent with WMO (2003) but are also forced to yield mixing ratios that meld smoothly into the measurement record. Future emissions are determined in order to yield banks consistent with IPCC/TEAP (2005).

**Bank:** The bank assumed to be in place at the start of the measurement record is set at such a value that the IPCC/TEAP (2005) bank for 2002 is attained; the future annual fractional bank release is adjusted so that the IPCC/TEAP (2005) bank for 2015 is attained.

---

**Approach for Specific Species**

---

Species	Description
CFC-11	<p><b>Production:</b></p> <p>1950-1985: WMO (2003)                      1986, 1989-2004: UNEP *                      1987-1988: McCulloch et al. (2001)                      2005-2006: Fixed at 2004 levels for Article 5(1) countries, with no other production                      2007-2009: Protocol limits on Article 5(1) countries, with no other production                      2010-on: No production</p> <p><b>Emission:</b></p> <p>1980-2004: Emissions calculated from observations                      2005-on: Emission is a constant fraction of the bank, determined to give a bank in 2015 consistent with IPCC/TEAP (2005)</p>
CFC-12	<p><b>Production:</b></p> <p>Same as CFC-11 except:                      1987-1988: Interpolated from 1986 and 1989 values                      2005-2006: Protocol limits for Article 5(1) countries with no other production</p> <p><b>Emission:</b></p> <p>Same formalism as for CFC-11</p>

---

## HALOCARBON SCENARIOS, ODPs, AND GWPs

**Table 8-4, continued.**

<b>Approach for Specific Species</b>	
CFC-113	<p>Production: Same formalism as for CFC-11</p> <p>Emission: 1986-2004: Emissions calculated from observations</p>
CFC-114	<p>Production: Same formalism as for CFC-11 except: 1987-1988: WMO (2003) 2005-2100: No production</p> <p>Emission: 1951-1959: WMO (2003) 1960-2100: Assume an annual fractional bank release of 0.4, chosen because it leads to bank results relatively close to those estimated by AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) in the 1980s</p>
CFC-115	<p>Production: Same formalism as for CFC-11 except: 1987-1988: WMO (2003) 2005-2100: No production</p> <p>Emission: 1950-2100: Assume an annual fractional bank release of 0.25, chosen because it leads to bank results relatively close to those estimated by AFEAS in the 1980s</p>
CCl <sub>4</sub>	<p>Production: Not considered due to gaps in our understanding of where much of the global emission originates</p> <p>Emission: 1951-1979: WMO (2003) (except the mixing ratio at the beginning of 1951 is assumed to be 37.0 rather than 35.0 (WMO, 2003) to achieve slightly better continuity with the measurements beginning in 1980 1980-2004: Emissions calculated from observations 2005-2015: Linear decrease from 65 ktons in 2005 (compared with 67.4 ktons calculated for 2004) to 0 in 2015 2015-2100: No emission</p>
CH <sub>3</sub> CCl <sub>3</sub>	<p>Production: Not considered</p> <p>Emission: 1950-1978: WMO (2003) 1979-2004: Emissions calculated from observations 2005-2009: Assume 2004 emissions because this value is lower than the limit in the Protocol (30% reduction relative to the 1998-2000 emission average; although the Protocol limits production and consumption and not emission, it is assumed that there is a negligibly small bank for this compound and that the limitations may be applied to emission) 2010-2014: Emission is 30% of the 1998-2000 average 2015-2100: No emission</p>
HCFC-22	<p>Production: 1950-1988: WMO (2003) 1989-2004: UNEP * 2005-2015: Linear interpolation of demand estimates from IPCC/TEAP (2005) for 2002 and 2015 2016-2030: Fixed at 2015 value</p>

Table 8-4, continued.

---

**Approach for Specific Species**


---

2030-2040: Linear interpolation from 2030 value to 0

## Emission:

1950-1992: Emissions calculated to yield mixing ratios consistent with WMO (2003) but moved 1 year earlier (the 1-year offset is to make the mixing ratios meld smoothly with the observations)

1993-2004: Emissions calculated from observations

2005-2100: Assume a bank release fraction of 0.13 (average of 2002-2004)

## Bank:

1993 WMO (2003) bank is reduced by 193 ktons from 1,036 ktons to obtain the IPCC/TEAP (2005) 2002 bank estimate; the bank in 2015 is 2,652 ktons compared with 1,879 ktons in IPCC/TEAP (2005); a much larger release fraction of 0.19 and increase in emissions in the near future would be needed to be consistent with the lower bank

---

**HCFC-141b Production:**

1989-2004: UNEP \*

2005-2015: Linear interpolation of demand estimates from IPCC/TEAP (2005) for 2002 and 2015

2016-2030: Fixed at 2015 value

2030-2040: Linear interpolation from 2030 value to 0

## Emission:

1993-2004: Emissions calculated from observations

2005-2100: Assume a bank release fraction of 0.05

## Bank:

1993 bank from WMO (2003) is not increased in spite of an apparent need for a larger 1993 bank to attain the 2002 IPCC/TEAP (2005) bank; the increase is not applied because the increase needed would lead to a 1993 bank too large to be consistent with estimated global production before 1993; hence the 2002 bank is 674 ktons, while the IPCC/TEAP (2005) estimate is 836 ktons; the 2015 bank is in agreement with the IPCC/TEAP (2005) bank

---

**HCFC-142b Production:**

1992-2004: UNEP \* (except for 1993)

1993: AFEAS data used because of unexplained drop in UNEP data for 1993

2005-2015: Linear interpolation of demand estimates from IPCC/TEAP (2005) for 2002 and 2015

2016-2030: Fixed at 2015 value

2030-2040: Linear interpolation from 2030 value to 0

## Emission:

1971-1992: WMO (2003) multiplied by 1.225 to attain a mixing ratio consistent with the start of the measurements in 1993

1993-2004: Emissions calculated from observations

2005-2100: Assume a bank release fraction of 0.08

## Bank:

1993 WMO (2003) bank is increased by 18 ktons to 103 ktons so the bank in 2002 is equal to the IPCC/TEAP (2005) 2002 bank; the bank release fraction of 0.08, which is consistent with the values estimated from 2002-2004 (0.085-0.089), leads to a bank in 2015 of 157 ktons, considerably lower than the 331 ktons estimated by IPCC/TEAP (2005)

---

**Halon-1211 Production:**

1989-2004: Corrected values from the Halons Technical Options Committee (HTOC) 2002 report (UNEP, 2003)

2005-2015: Linear interpolation of demand estimates from IPCC/TEAP (2005) for 2002 and 2015

2016-2030: Fixed at 2015 value

2030-2040: Linear interpolation from 2030 value to 0

**HALOCARBON SCENARIOS, ODPs, AND GWPs**

**Table 8-4, continued.**

**Approach for Specific Species**

	<p>Emission:            1950-1992: WMO (2003) multiplied by 1.02 to attain a mixing ratio in 1993 consistent with measurements            1993-2004: Emissions calculated from observations            2005-2100: Assume a bank release fraction of 0.07</p> <p>Bank:            2002 bank of 122 ktms is only 3 ktms below the IPCC/TEAP (2005) bank; the bank release fraction of 0.07, which is consistent with the release fraction from 1993-2004, leads to a bank in 2015 of 52 ktms compared with 31 ktms from IPCC/TEAP (2005); the 2002 bank of 125 ktms is larger than the 72 ktms in WMO (2003)</p> <p>Note that corrected data are used for banks and emissions of halon-1211 (TEAP, 2005) and hence differ from the data reported in IPCC/TEAP (2005). The 2002 emission data are changed from 17 to 8 ktms per year.</p>
Halon-1301	<p>Production:            1986-2009: HTOC 2002 report (UNEP, 2003)            2010-2100: No production</p> <p>Emission:            1950-1995: WMO (2003)            1996-2100: Assume a bank release fraction of 0.05 (leads to mixing ratios between NOAA/ESRL and AGAGE observations)</p> <p>Bank:            2002 and 2015 banks agree with IPCC/TEAP (2005)</p>
Halon-1202	Same as WMO (2003)
Halon-2402	Same as WMO (2003)
CH <sub>3</sub> Br	<p>Production:            Natural production/emission assumed to be 146 ktms            2005: Natural plus 10.7 ktms for quarantine/pre-shipment plus 14.1 ktms for critical uses plus 0.5 ktms for Article 5(1) production (same as 2004 reported to UNEP)            2006-2014: Same as 2005 but 13.0 ktms of critical uses            2015-2100: Natural plus 10.7 ktms for quarantine/pre-shipment</p> <p>Emission:            1950-2004: Emissions calculated from surface observations and South Pole firm observations (using global lifetime of 0.7 years, Table 8-1)            2005-2100: Emission equal to 0.88 times the anthropogenic production plus natural emissions; this combination of anthropogenic and natural emissions, constrained by the total emissions derived from observations of concentrations, leads to an anthropogenic fraction of the total production of 0.30 in 1992, in agreement with Montzka et al. (2003).</p> <p>Bank:            No bank considered</p>
CH <sub>3</sub> Cl	<p>Emission:            Same as WMO (2003); assumed mostly natural (i.e., no future changes due to anthropogenic activity)            1950-1995: Emissions calculated from firm observations at the South Pole            1996-2100: Emissions held constant at 1995 levels</p>

\* Estimated in cases in which reporting is not complete or reporting is made in compound classes rather than individually. The production data per species per year are obtained from UNEP (UNEP, 2005) and are consistent with the totals per class of species as usually reported by UNEP.

enough to have significant implications concerning the environmental benefits of reusing or destroying CFCs contained in existing equipment and products. Increases in the projected HCFC-22 emissions, due to larger reported (to UNEP) historic production in developing countries in 2000-2004 than projected in the Ab scenario, and expectations of greater future use based on IPCC/TEAP (2005), are also important.

While the historic emissions calculated with the 1-box model for this Assessment are completely constrained by the observations, emissions from Clodic and Palandre (2004) and IPCC/TEAP (2005) are based exclusively on estimates of the banks and bank release fractions and can be substantially different from those estimated from mixing ratio observations. As previously stated, for some species that have significant foam applications, i.e., CFC-11, HCFC-141b, and HCFC-142b, these emission differences are greater than a factor of two, with the estimated bottom-up emission underpredicting those derived from observed mixing ratio changes. In Table 1-7 of Chapter 1, an uncertainty range for the emissions in 2003 is given based on an uncertainty range in the lifetimes of the ODSs and calculations with the 12-box model. The uncertainty ranges of the inferred 2003 emissions are somewhat larger than those given in IPCC/TEAP (2005), but the IPCC ranges were due to model differences and to the variations in the trends of the different global networks, rather than different assumed lifetimes. Nevertheless, the top-down emissions in scenario A1 and bottom-up emissions of IPCC/TEAP (2005) for CFC-11, HCFC-141b, and HCFC-142b cannot be reconciled taking these uncertainties in emissions into account. These differences illustrate that there is a need for greater understanding regarding the possible shortcomings of the bottom-up approach and the differences between it and past approaches. The discrepancies are large enough to cast some doubt on projected future emissions that are based on the published bottom-up results alone. Section 8.3.4 contains a more extensive discussion of uncertainties.

### 8.3.2.2 MIXING RATIOS

The projected ODS mixing ratios for the baseline scenario are mostly consistent with those of the previous Assessment before the year 2002 because the previous Assessment's past mixing ratios were based on observations, and here observations are used as a direct constraint (see Figure 8-2). The observations are taken primarily from the Earth System Research Laboratory / Global

Monitoring Division (ESRL/GMD) (formerly Climate Monitoring and Diagnostics Laboratory, CMDL) (Montzka et al., 1999) and Advanced Global Atmospheric Gases Experiment (AGAGE) networks (Prinn et al., 2005) (and include the University of East Anglia observations for halon-1211), and the calibration factors were calculated in a similar manner as in Table 1-15 of WMO (2003). After correcting for calibration differences, the mean mixing ratios of the ESRL/GMD and AGAGE networks are used for temporally overlapping periods for the CFCs,  $\text{CH}_3\text{CCl}_3$ , and for  $\text{CCl}_4$ . For periods before any overlap exists, the ratios of the measurements are used to extend the record backward in time in a consistent manner. The average of the December and January observations are assumed to represent the mixing ratios at the start of the year, with the mixing ratios for the rest of the year calculated from estimated emissions and lifetimes. Although the model is run in 0.1-year time steps, yearly observations are used instead of monthly ones in order to avoid the impact of seasonal variability on the inferred emissions, which are assumed to be constant throughout each year. Calculated mixing ratios are tabulated in Table 8-5 for each of the considered halocarbons from 1955 through 2100. The yearly observations used are indicated in the table by the shaded regions.

Time series are shown in Figure 8-2 for the current A1 scenario and the previous Ab scenario. There are some differences between mixing ratios of this Assessment compared with the previous one for the period 2001-2004, but the greatest differences are found in the future projections. The HCFC-22 projection exhibits the most striking differences compared with the previous Assessment's scenario Ab projection with a peak mixing ratio over 150 ppt higher and peaking more than 20 years later. In contrast, HCFC-141b, HCFC-142b, and halon-1301 exhibit decreases in near-term projected mixing ratios compared with the Ab scenario, due to the decrease in observed growth rates from 2001 through 2004 and the expectation of lower future emissions for these species (Figure 8-1). Due to the increased emissions discussed in Section 8.3.2.1, future CFC-11 and CFC-12 mixing ratios also exhibit modest, but important, increases compared with the previous Assessment. Carbon tetrachloride decreases more slowly in A1 due to greater emission in the coming decade, with the increased emission based on the uncertain source of much of the global  $\text{CCl}_4$  emission (see Chapter 1) and the slow decline of annual emissions over the past 15 years.

**Table 8-5. Mixing ratios (ppt) of the ODSs considered in scenario A1.** Values are for the beginning of the corresponding year. Potentially important short-lived gases that may currently contribute 3-8 ppt of stratospheric bromine and ~50 ppt of stratospheric chlorine (see Chapter 2) are not shown in the table.

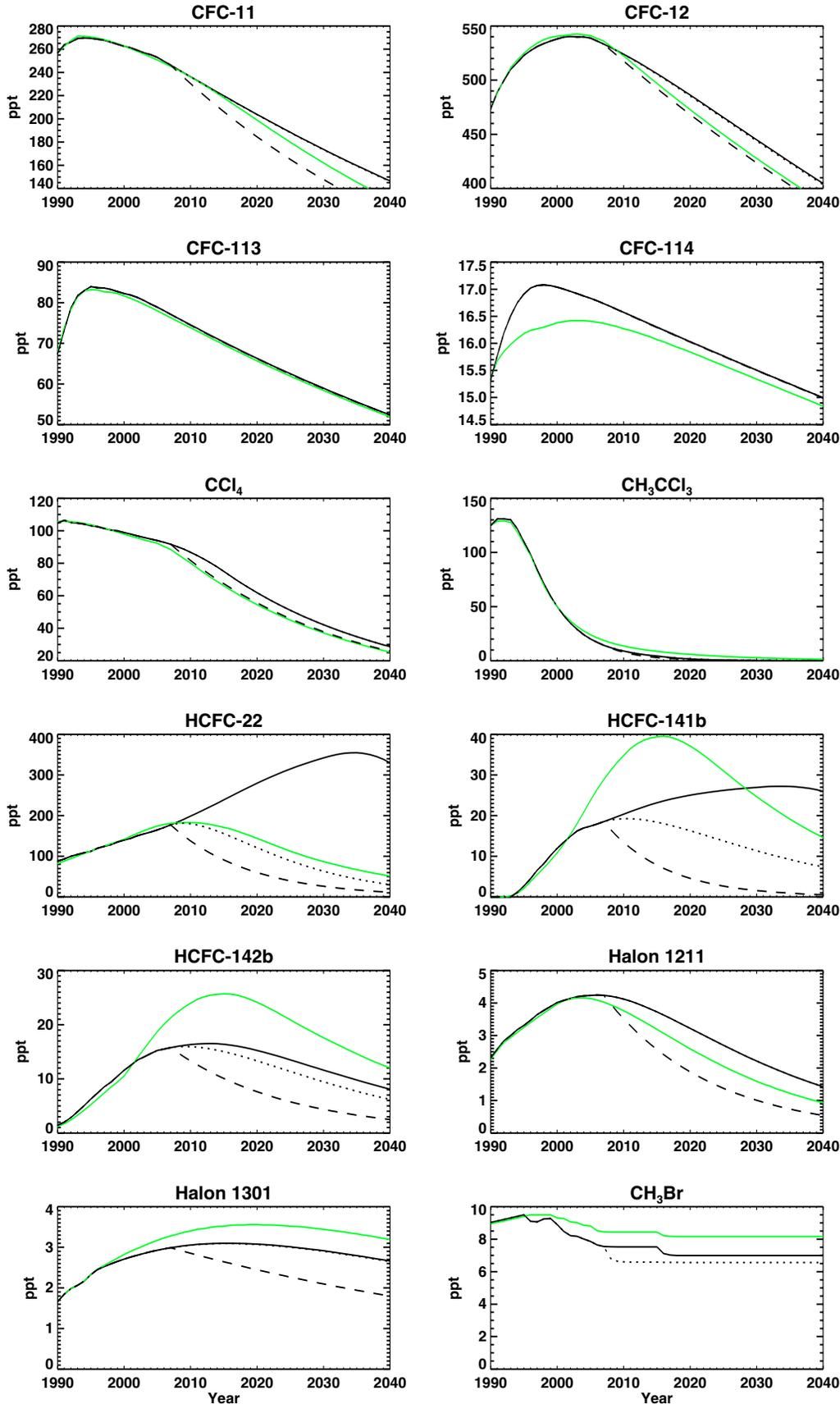
	CFC-11		CFC-113		CFC-114		CFC-115		CCl <sub>4</sub>		CH <sub>3</sub> CCl <sub>3</sub>		HCFC-22		HCFC-141b		Halon-142b		Halon-1211		Halon-1301		Halon-2402		CH <sub>3</sub> Br		CH <sub>3</sub> Cl	
1955	3.3	14.3	1.3	2.6	0.0	0.0	42.4	0.1	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.13	492.1	7.13	492.1
1960	9.5	29.5	1.9	3.9	0.0	0.0	52.1	1.5	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.30	510.3	7.30	510.3
1965	23.5	58.8	3.1	5.1	0.0	0.0	64.4	4.7	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.49	528.1	7.49	528.1
1970	52.8	114.3	5.5	6.5	0.2	0.2	75.9	16.3	12.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.71	539.9	7.71	539.9
1975	106.1	203.1	10.4	8.2	0.6	0.6	85.5	40.0	23.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.97	545.8	7.97	545.8
1980	163.7	294.9	20.1	10.3	1.5	1.5	93.4	82.0	40.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.27	548.3	8.27	548.3
1981	173.4	313.6	22.9	10.8	1.8	1.8	94.6	89.9	44.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.34	548.6	8.34	548.6
1982	182.3	329.8	26.0	11.3	2.1	2.1	95.3	94.5	48.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.41	548.9	8.41	548.9
1983	189.3	346.5	29.2	11.7	2.4	2.4	96.5	98.2	52.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.48	549.1	8.48	549.1
1984	198.2	363.5	32.8	12.2	2.8	2.8	98.1	103.3	56.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.55	549.3	8.55	549.3
1985	207.5	381.5	38.1	12.7	3.2	3.2	99.6	108.1	60.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.62	549.4	8.62	549.4
1986	216.7	398.1	41.8	13.2	3.6	3.6	100.1	111.1	65.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.70	549.5	8.70	549.5
1987	228.9	419.2	46.8	13.7	4.0	4.0	102.1	113.2	69.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.78	549.6	8.78	549.6
1988	240.9	437.7	54.3	14.3	4.4	4.4	102.8	119.4	75.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.86	549.7	8.86	549.7
1989	248.9	458.8	61.6	14.8	4.8	4.8	104.1	124.0	81.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.94	549.8	8.94	549.8
1990	256.6	473.5	67.4	15.3	5.3	5.3	104.8	124.9	87.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.03	549.8	9.03	549.8
1991	263.7	489.1	73.2	15.8	5.8	5.8	106.4	130.9	93.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.12	549.9	9.12	549.9
1992	266.2	499.7	78.7	16.2	6.3	6.3	105.1	130.9	99.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.21	549.9	9.21	549.9
1993	269.3	509.9	81.7	16.5	6.7	6.7	104.7	130.1	104.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.30	549.9	9.30	549.9
1994	269.7	516.3	83.0	16.8	7.2	7.2	104.0	121.9	108.8	1.1	5.0	3.9	3.00	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	9.40	549.9	9.40	549.9
1995	269.3	522.8	84.0	16.9	7.6	7.6	103.1	109.9	112.1	2.7	6.3	6.3	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31	9.50	550.0	9.50	550.0
1996	268.6	527.3	83.7	17.0	8.0	8.0	102.5	98.3	119.6	4.5	7.4	7.4	3.47	3.47	3.47	3.47	3.47	3.47	3.47	3.47	3.47	3.47	3.47	3.47	9.10	550.0	9.10	550.0
1997	267.8	531.0	83.6	17.1	8.2	8.2	101.4	84.2	124.3	6.6	8.5	8.5	3.64	3.64	3.64	3.64	3.64	3.64	3.64	3.64	3.64	3.64	3.64	3.64	9.06	550.0	9.06	550.0
1998	266.1	533.8	83.3	17.1	8.5	8.5	100.4	71.5	128.4	8.2	9.4	9.4	3.77	3.77	3.77	3.77	3.77	3.77	3.77	3.77	3.77	3.77	3.77	3.77	9.25	550.0	9.25	550.0
1999	264.3	536.1	82.8	17.1	8.6	8.6	99.9	59.7	135.0	10.2	10.5	10.5	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	9.27	550.0	9.27	550.0
2000	262.6	538.1	82.3	17.0	8.7	8.7	98.8	49.9	139.8	11.9	11.6	11.6	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	4.01	8.90	550.0	8.90	550.0
2001	261.2	539.7	81.9	17.0	8.8	8.8	98.0	41.6	144.1	13.5	12.5	12.5	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08	8.48	550.0	8.48	550.0
2002	259.0	540.2	81.3	17.0	8.9	8.9	96.8	34.6	150.8	14.9	13.5	13.5	4.14	4.14	4.14	4.14	4.14	4.14	4.14	4.14	4.14	4.14	4.14	4.14	8.22	550.0	8.22	550.0

Table 8-5, continued.

	CFC-11		CFC-113		CFC-115		CH <sub>3</sub> CCl <sub>3</sub>		HCFC-22		HCFC-141b		Halon-142b		Halon-1211		Halon-1202		Halon-1301		CH <sub>3</sub> Br		CH <sub>3</sub> Cl
	CFC-11	CFC-12	CFC-113	CFC-114	CFC-115	CCl <sub>4</sub>	CH <sub>3</sub> CCl <sub>3</sub>	HCFC-22	HCFC-141b	HCFC-142b	Halon-1211	Halon-1202	Halon-1301	Halon-2402	CH <sub>3</sub> Br	CH <sub>3</sub> Cl							
2003	256.9	539.9	80.6	16.9	9.0	95.8	28.9	155.1	16.2	14.1	4.20	0.03	2.85	0.39	8.17	550.0							
2004	255.2	539.9	79.7	16.9	9.0	94.9	24.0	159.8	17.0	14.7	4.22	0.03	2.89	0.38	8.01	550.0							
2005	253.0	538.9	78.9	16.8	9.1	94.0	20.1	164.7	17.4	15.2	4.24	0.02	2.93	0.37	7.86	550.0							
2006	249.6	536.1	78.0	16.8	9.1	92.9	16.9	170.7	17.9	15.5	4.25	0.02	2.96	0.36	7.64	550.0							
2007	246.3	533.3	77.2	16.7	9.1	91.7	14.3	177.1	18.5	15.8	4.24	0.02	2.99	0.35	7.55	550.0							
2008	242.9	530.3	76.3	16.7	9.1	90.2	12.2	183.9	19.1	16.0	4.21	0.01	3.01	0.34	7.53	550.0							
2009	239.6	527.2	75.4	16.6	9.1	88.6	10.4	191.1	19.7	16.2	4.17	0.01	3.04	0.32	7.53	550.0							
2010	236.3	523.9	74.6	16.6	9.1	86.8	9.0	198.5	20.4	16.3	4.12	0.01	3.05	0.31	7.52	550.0							
2015	219.8	506.0	70.3	16.3	9.1	75.0	4.4	238.7	23.2	16.4	3.73	0.00	3.10	0.26	7.52	550.0							
2020	203.8	486.2	66.3	16.0	9.1	61.9	1.6	279.7	25.0	15.3	3.22	0.00	3.08	0.21	6.99	550.0							
2025	188.4	465.6	62.5	15.8	9.1	51.1	0.6	314.8	26.2	13.5	2.70	0.00	3.01	0.17	6.99	550.0							
2030	173.7	444.9	59.0	15.5	9.0	42.1	0.2	342.1	27.0	11.6	2.22	0.00	2.91	0.13	6.99	550.0							
2035	159.7	424.5	55.6	15.3	9.0	34.8	0.1	354.8	27.2	9.8	1.79	0.00	2.79	0.10	6.99	550.0							
2040	146.5	404.7	52.4	15.0	9.0	28.7	0.0	330.0	26.0	8.1	1.42	0.00	2.66	0.08	6.99	550.0							
2045	134.2	385.4	49.4	14.8	9.0	23.7	0.0	269.6	23.2	6.6	1.12	0.00	2.52	0.06	6.99	550.0							
2050	122.7	367.0	46.6	14.5	8.9	19.5	0.0	203.7	19.7	5.3	0.88	0.00	2.38	0.05	6.99	550.0							
2055	112.0	349.3	43.9	14.3	8.9	16.1	0.0	147.2	16.3	4.2	0.68	0.00	2.24	0.04	6.99	550.0							
2060	102.1	332.4	41.4	14.0	8.9	13.3	0.0	103.5	13.2	3.3	0.53	0.00	2.10	0.03	6.99	550.0							
2065	92.9	316.3	39.1	13.8	8.9	11.0	0.0	71.4	10.6	2.6	0.40	0.00	1.97	0.02	6.99	550.0							
2070	84.5	300.9	36.8	13.6	8.8	9.0	0.0	48.7	8.4	2.0	0.31	0.00	1.84	0.02	6.99	550.0							
2075	76.7	286.3	34.7	13.4	8.8	7.5	0.0	32.9	6.6	1.6	0.23	0.00	1.71	0.01	6.99	550.0							
2080	69.6	272.3	32.7	13.1	8.8	6.2	0.0	22.1	5.2	1.2	0.18	0.00	1.60	0.01	6.99	550.0							
2085	63.1	259.1	30.9	12.9	8.8	5.1	0.0	14.8	4.1	0.9	0.13	0.00	1.48	0.01	6.99	550.0							
2090	57.1	246.5	29.1	12.7	8.7	4.2	0.0	9.8	3.2	0.7	0.10	0.00	1.38	0.01	6.99	550.0							
2095	51.7	234.4	27.4	12.5	8.7	3.5	0.0	6.5	2.5	0.6	0.08	0.00	1.28	0.01	6.99	550.0							
2100	46.7	223.0	25.9	12.3	8.7	2.9	0.0	4.3	1.9	0.4	0.06	0.00	1.19	0.00	6.99	550.0							

Note: Areas are shaded for compounds in years when mixing ratio values are forced to equal global estimates calculated from observations. Global means for CH<sub>3</sub>Br and CH<sub>3</sub>Cl before 1996 were derived from South Pole firm air observations (Butler et al., 1999) and based on surface observations of CH<sub>3</sub>Br after 1996 (Montzka et al., 2003). All other shaded areas are from atmospheric observations from one or more measurement networks (see text). Halon-1301 values used in this scenario fall between the global estimates made from observations of the NOAA/ESRL and AGAGE networks.

HALOCARBON SCENARIOS, ODPs, AND GWPs



**Figure 8-2.** Projected mixing ratios of selected halocarbons for scenarios A1 (solid black), Ab (green, previous Assessment), E0 (dashed curve), and P0 (dotted curve). Note that for many of the gases, little or no future production is included in the A1 scenario, so the P0 curve is obscured by the A1 curve. For CH<sub>3</sub>Br, the E0 and P0 curves are identical.

### 8.3.2.3 EQUIVALENT EFFECTIVE STRATOSPHERIC CHLORINE

The equivalent effective stratospheric chlorine (EESC) index (see Daniel et al., 1995; WMO, 2003) has been used in past Assessments and is summarized in Box 8-1. It is used as a measure of the amount of chlorine and bromine available in the stratosphere to destroy ozone. Here, we set  $f_{CFC-11}$ , the absolute fractional release value for CFC-11 (Equation 1 of Box 8-1), to be 0.84 as was done in the previous Assessment, with the  $\rho$  values assumed to be equal to the surface mixing ratios. This factor was incorrectly stated to be 0.8 in footnote “a” of Table 1-4 in the previous Assessment. It should also be noted that the  $CH_3Br$  mixing ratio at the tropopause may be less than the surface mixing ratio by a non-negligible amount due to its relatively large tropospheric loss (see Chapter 2); this would lead to

an additional reduction in the EESC contribution from  $CH_3Br$  that is not considered in this chapter. Newman et al. (2006) have extended the definition of EESC in order for it to correspond to the actual amount of inorganic chlorine and bromine in various stratospheric locations by applying location-appropriate age spectra, fractional release values, and “ $f_{CFC-11}$ ” values. We do not consider the variation of EESC with stratospheric location, except in accounting for the older age of air in the Antarctic polar vortex as discussed below. Instead, we continue using EESC as an index that is only proportional to overall stratospheric inorganic chlorine and bromine. Very short-lived species are currently not included in the EESC calculation. In the future, as our knowledge of the very short-lived bromocarbon source gases improves (see Chapter 2), it may be warranted to link EESC directly with spatially varying inorganic chlorine and bromine in order to assess the importance of

#### Box 8-1. Equivalent Effective Stratospheric Chlorine (EESC)

Due to the established relationship between stratospheric ozone depletion and inorganic chlorine and bromine abundances, the temporal evolution of chlorine- and bromine-containing source gases is an important indicator of the potential effects of anthropogenic activity on the health of stratospheric ozone. Indices have been developed to demonstrate this halogen evolution in a simple manner. They account for the greater per-atom potency of stratospheric bromine (Br) compared with chlorine (Cl) in its ozone destructiveness with a constant factor,  $\alpha$  (Section 8.2.2.3), and include the varying rates at which Cl and Br will be released in the stratosphere from different source gases.

EESC provides a simple index that relates the time evolution of long-lived surface abundances of ODSs with the ozone-destructive ability of stratospheric halogens that come from these long-lived source gases (WMO, 1995, 1999, 2003). Contributions of very short-lived chlorine- and bromine-containing sources gases and of tropospheric inorganic halogens generally have been neglected. EESC is defined as

$$EESC(t) = f_{CFC-11} \left[ \sum_{\substack{\text{Cl-containing} \\ \text{halocarbons}}} n_i \frac{f_i}{f_{CFC-11}} \rho_{i,entry} + \alpha \sum_{\substack{\text{Br-containing} \\ \text{halocarbons}}} n_i \frac{f_i}{f_{CFC-11}} \rho_{i,entry} \right] \quad (1)$$

(Daniel et al., 1995), where  $n$  is the number of chlorine or bromine atoms in the source gas,  $f_i/f_{CFC-11}$  represents the efficiency of the stratospheric halogen release relative to that of CFC-11, denoted by  $f_{CFC-11}$  (Section 8.2.2.2), and  $\rho_{i,entry}$  is the tropospheric mixing ratio of source gas  $i$  when it entered the stratosphere. Traditionally,  $\rho_{i,entry}$  is calculated assuming a simple time lag  $\Gamma$  from the surface observations, i.e.,

$$\rho_{i,entry}(t) = \rho_i(t - \Gamma) \quad (2)$$

where  $\rho_i(t)$  is the surface mixing ratio at time  $t$ . In WMO (2003), EESC was estimated assuming  $\Gamma = 3$  years (typical of the lower, midlatitude stratosphere) to obtain a value appropriate for relating to midlatitude-averaged ozone loss. Effective equivalent chlorine (EECl) (Montzka et al., 1996) is a quantity similar to EESC, but includes no consideration of the transport lag time.

To retain the simplicity of the EESC index, several assumptions are generally made in its calculation. One such assumption is that the stratospheric entry mixing ratio for a given time is taken to be the surface mixing ratio at that time. This could be an overestimate of the EESC contribution for shorter-lived gases, like  $CH_3Br$ , whose abundance may be reduced before reaching the tropopause. In Montzka et al. (2003), this issue has been addressed by reducing the surface mixing ratio by 7% in the calculation of EESC. A second assumption generally made in EESC calculations

Continued, next page.

**Box 8-1, continued.**

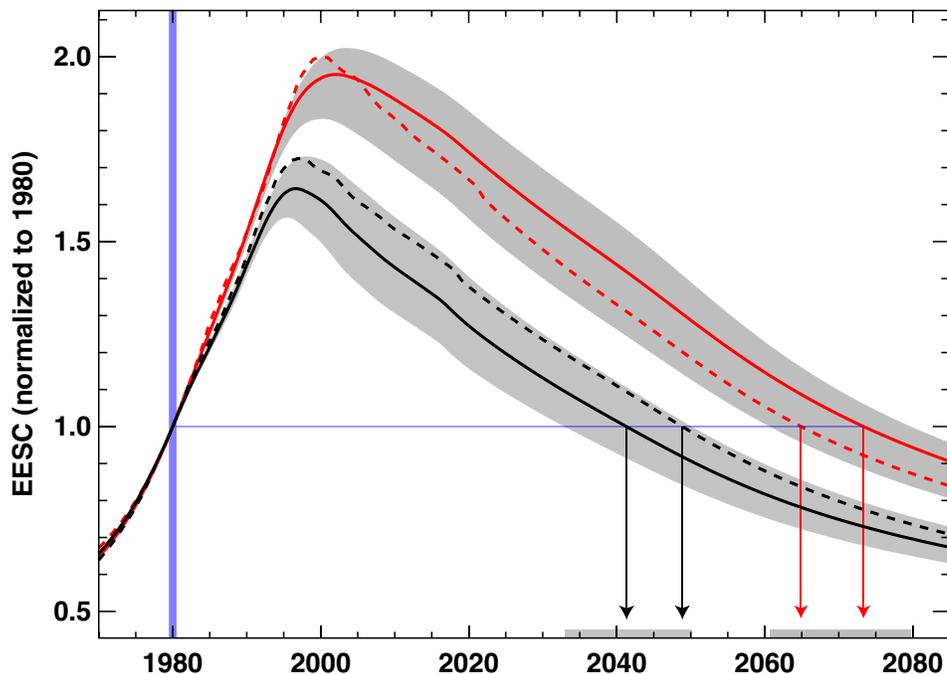
is the neglect of the transport time from the surface to the tropopause. Although the particular location of the surface emission affects the transport time to the tropopause, this is generally not considered.

Newman et al. (2006) extended the method of calculating EESC to account for the lack of a single transit time from the surface to a stratospheric location (i.e., stratospheric air is composed of air characterized by a range, or spectrum, of transit times, or ages) and that the fractional release values depend on the age of air. In Newman et al. (2006),  $\rho_{i,entry}$  is calculated using

$$\rho_{i,entry}(t) = \int_{-\infty}^t \rho_i(t')G(t-t')dt' \tag{3}$$

where  $G(t)$  is the age-spectrum, assumed to be an inverse Gaussian function with mean  $\Gamma$  and width  $\Delta$  (see Equation 9 of Waugh and Hall, 2002), and  $f_i = f_i(\Gamma)$ . This reduces to the traditional EESC calculation if the mean age  $\Gamma = 3$  yrs and the width  $\Delta = 0$ , i.e., (3) reduces to (2) when  $\Delta = 0$ . Including an age spectrum does not affect the EESC evolution when the temporal trend is constant, but acts to smooth changes over time when the trend is varying. Specifically, when an age spectrum is included, the period near when the maximum EESC occurs is characterized by a “flutter” or less peaked EESC time series.

The figure compares calculations of EESC, normalized by the 1980 value, for midlatitude and polar regions and illustrates some of the important sensitivities. The dashed lines show the EESC evolution used in Chapter 8 for midlatitudes (black) and inside the polar vortex in the lower stratosphere (red) (i.e., for  $\Gamma = 3$  yrs and  $\Delta = 0$  yrs for midlatitudes, and  $\Gamma = 6$  yrs and  $\Delta = 0$  yrs for the vortex). The solid lines show the same calculations using the fractional release values from Newman et al. (2006) and the same mean ages as the dashed lines, but with  $\Delta$  equal to half the mean age in each case. The shaded regions show the sensitivity of the calculations using the Newman et al. fractional release values to a  $\pm 1$ -year mean age and with  $\Delta$  always equal to half the mean age (e.g., for  $\Gamma = 2$  yrs and  $\Delta = 1$  yr, to  $\Gamma = 4$  yrs and  $\Delta = 2$  yrs for the midlatitude case). Using a larger value of  $\Gamma$  results in a shift in curves and leads to a much later recovery date, but does not change the EESC shape. Compared with the midlatitude recovery, the polar recovery time is delayed by much more than the 3-year older age of air because the magnitude of the slope of the EESC curve is projected to be much smaller in the mid-21<sup>st</sup> century than it was in 1980s. The inclusion of the age spectrum width in the polar calculation is the reason for the smoother EESC peak period but has little effect during periods when EESC is changing approximately linearly with time, and hence affects the time of return to 1980 levels only slightly.

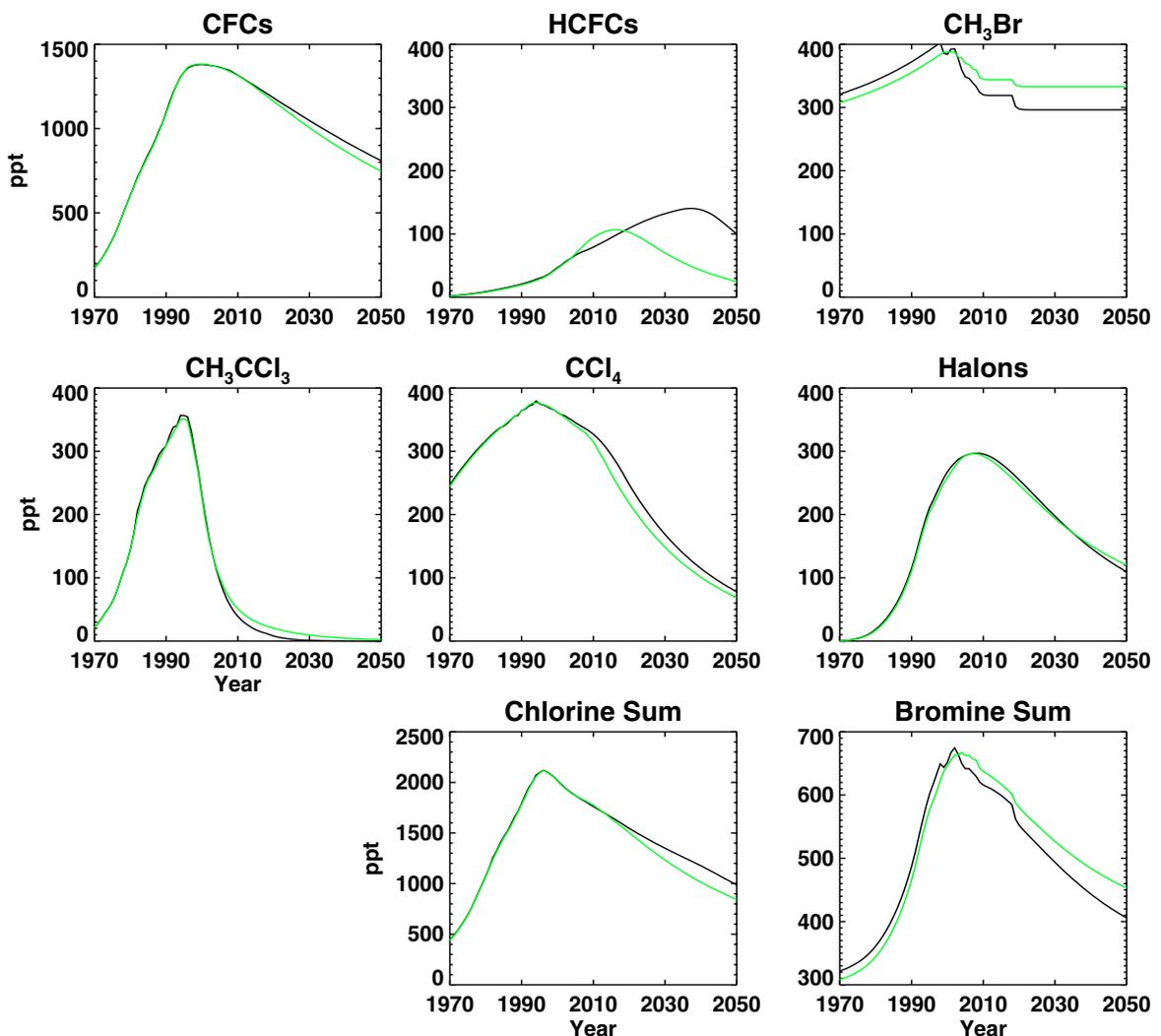


these very short-lived species relative to long-lived source gases for ozone depletion.

As in previous Assessments, the year EESC returns to its 1980 levels is one metric used to compare different scenarios. The year 1980 is chosen because this is the approximate date when midlatitude and Antarctic ozone depletion has been observed to begin. It generally has been assumed that if all other atmospheric parameters and processes remain constant, ozone depletion relates linearly to EESC above a certain threshold level. An exception to this relationship is Antarctic ozone depletion. Springtime depletion became so great around 1990 that there was not enough ozone left in the lower stratosphere for the column

ozone amount to continue to follow a linear relationship with EESC. So it is assumed here (in the calculations of indirect GWPs, Section 8.5) that no additional Antarctic ozone destruction occurs for EESC values above 1990 levels. The second metric that has been used to compare scenarios is the integrated EESC value above the 1980 level, integrated from 1980 or the current time until EESC returns to the 1980 level. This metric is meant to represent the cumulative ozone depletion due to ODSs over the specified time frame.

The contributions of the various halocarbon groups to EESC for scenario A1, as well as for scenario Ab of the previous Assessment, are shown in Figure 8-3. The CFCs continue to be the dominant source of EESC, although as



**Figure 8-3.** Contributions of halocarbon groups to global EESC for this Assessment (A1 scenario, black lines) and the previous Assessment (Ab scenario, green lines). The “chlorine sum” and “bromine sum” represent the total EESC from these particular chlorine and bromine long-lived source gases. EESC values for CH<sub>3</sub>Br, the halons, and the bromine sum for this Assessment are scaled by 45/60 to eliminate the effect of the change in the  $\alpha$  value, for easier comparison with the previous Assessment values.

## HALOCARBON SCENARIOS, ODPs, AND GWPs

a group their contribution has begun to decrease, driven mostly by the decline of CFC-11. In terms of EESC, the most striking differences between the A1 and Ab scenarios are the HCFCs. As discussed in Sections 8.3.2.1 and 8.3.2.2, this increasing importance of the HCFCs is primarily due to the increase in expected future production and emission of HCFC-22 (Table 8-4). The updates to future emissions of CFCs and HCFCs lead to slight increases in the importance of these ODS groups to EESC in the future. Updates to the fractional halogen release values of the halons lead to a slightly larger contribution of these compounds. Estimated CH<sub>3</sub>Br abundances are also noticeably different from WMO (2003). The differences from 1996 through 2004 arise because of the availability of new global surface data (Montzka et al., 2003, and updates). After that period, differences arise because of the larger assumed anthropogenic fraction of CH<sub>3</sub>Br emission compared with WMO (2003) (30% compared with 20%), also based on Montzka et al. (2003). Overall, the updates to the future ODS emissions projections and the increase in the estimated value for  $\alpha$  lead to a later “recovery” of midlatitude-relevant EESC, defined here as a return to pre-1980 values, by about 5 years.

In past Assessments, quantification of midlatitude-relevant EESC was used exclusively. These calculations assumed a lag of 3 years between surface and stratospheric mixing ratios and assumed a value for  $\alpha$  of 45. However, it is known that the age of air in the wintertime polar vortex is greater than 3 years (Andrews et al., 2001; Daniel et al., 1996; Harnisch et al., 1999), and there are indications that the value of  $\alpha$  should be larger, due to the stronger coupling of bromine monoxide (BrO) with chlorine monoxide (ClO) (Chipperfield and Pyle, 1998). Both of these points act to delay the halocarbon recovery of the polar vortex compared with midlatitudes. Consideration of the spectrum of ages that make up wintertime vortex air can further delay halocarbon recovery (Newman et al., 2006). The time lag increase is expected to be particularly important because of the fast increase in halocarbon abundances in the 1980s and the relatively slow decline expected in the future due to halocarbon lifetimes of decades. If a time lag is assumed to be 6 years and a value of  $\alpha$  of 65 (Chipperfield and Pyle, 1998), the year of EESC recovery for Antarctic conditions is 2065, more than 15 years later compared with the midlatitude EESC recovery; the time lag increase is responsible for almost 13 of the 15 years, with the change in  $\alpha$  responsible for the rest. Due to the large sensitivity of the EESC recovery to the age of air, all scenarios will be performed for midlatitude-relevant and polar vortex-relevant EESC. Newman et al. (2006) have also shown that the use of a simple lag can lead to

errors in estimated EESC, particularly near the peak period. However, because there is little difference in the recovery date when using a simple lag or a more complicated age spectrum, and because there is no agreement on a particular globally averaged age spectrum to use, we continue to use a simple time lag in this Assessment.

### 8.3.3 Alternative Projections

#### 8.3.3.1 EMISSIONS

The alternative hypothetical cases used to examine the relative environmental effects of reducing future production and emissions of groups of halocarbons are compared in Table 8-6 and fall into three categories, each of which is based on the baseline A1 scenario: (1) “no future emission” cases (E0); (2) “no future production” cases (P0); and (3) cases of the full capture and destruction of the 2007 bank (B0). Assumptions of the alternative projections lead to various decreases in future emissions when compared with the baseline scenario. The hypothetical elimination of all future emissions (E0) represents the greatest possible reduction in future abundances. The hypothetical elimination of future production (P0) allows the ODSs currently residing in banks to continue to be released to the atmosphere as they would in the baseline scenario. The projections that consider the full capture and destruction of the 2007 bank (B0) complement the “no production” cases in that the full 2007 bank is destroyed in a manner that releases no ODS to the atmosphere; future production and the resulting future buildup of banks is allowed to continue, however. This expected future production is small for the CFCs and halons, but significant for the HCFCs. A case consistent with the mitigation scenario presented in IPCC/TEAP (2005) is assessed to illustrate the importance of emissions reductions from this carefully developed scenario on the future evolution of EESC. The mitigation scenario has a significant effect only on the banks of HCFC-22, HCFC-123, and HFCs in 2015 (the latter two are not considered in the cases or scenarios of this chapter).

#### 8.3.3.2 MIXING RATIOS

The calculated mixing ratios from 1990 through 2040 are shown in Figure 8-2 for the E0 and P0 cases in addition to the previously discussed A1 and Ab scenarios. These calculations suggest that all ODSs considered here, except for the HCFCs and possibly halon-1301 have already reached their peak mixing ratios. The HCFCs are expected to reach peak abundances between 2010 and

**Table 8-6. Comparison of scenarios and hypothetical cases <sup>a</sup>: the year when EESC drops below the 1980 value for both midlatitude and polar vortex cases, and integrated EESC differences (midlatitude case) relative to the baseline (A1) scenario.** Note that the polar recovery times have not been given in previous Assessments; interpretation of any comparison between these numbers and recovery times given in previous Assessments requires an understanding of the large role played by the different transport times from the troposphere to the stratospheric midlatitude and polar vortex regions.

Scenario and Cases	Percent Difference in integrated EESC relative to baseline scenario for the midlatitude case		Year (x) when EESC is expected to drop below 1980 value	
	Midlatitude		Antarctic vortex <sup>b</sup>	
	$\int_{1980}^x EESC dt$	$\int_{2007}^x EESC dt$		
<b>Scenarios</b>				
A1: Baseline scenario			2048.9	2065.1
<b>Cases <sup>a</sup> of zero production from 2007 onward of:</b>				
P0: All ODSs	-8.0	-17.1	2043.1	2060.3
CFCs	-0.1	-0.3	2048.8	2065.0
Halons	-0.2	-0.5	2048.8	2065.1
HCFCs	-5.5	-11.8	2044.4	2062.2
Anthropogenic CH <sub>3</sub> Br	-2.4	-5.1	2047.9	2063.7
<b>Cases <sup>a</sup> of zero emissions from 2007 onward of:</b>				
E0: All ODSs	-19.4	-41.7	2034.0	2049.9
CFCs	-5.3	-11.5	2045.0	2060.3
CH <sub>3</sub> CCl <sub>3</sub>	-0.1	-0.2	2048.9	2065.1
Halons	-6.7	-14.4	2045.6	2061.9
HCFCs	-7.3	-15.7	2043.7	2061.8
CCl <sub>4</sub>	-1.3	-2.9	2048.5	2064.9
Anthropogenic CH <sub>3</sub> Br	-2.4	-5.1	2047.9	2063.7
<b>Cases <sup>a</sup> of full recovery of the 2007 banks of:</b>				
B0: All ODS	-12.9	-27.8	2040.8	2056.7
CFCs	-5.2	-11.3	2045.1	2060.4
Halons	-6.7	-14.3	2045.7	2062.0
HCFCs	-1.9	-4.1	2048.4	2064.8
<b>CH<sub>3</sub>Br sensitivity:</b>				
Same as A1, but CH <sub>3</sub> Br anthropogenic emissions set to 20% in 1992 <sup>c</sup>	3.1	6.6	2050.6	2067.7
Same as A1, but zero QPS production from 2015 onward	-1.5	-3.2	2047.9	2063.7
Same as A1, but critical-use exemptions continued at 2006 level	1.9	4.0-4.7	2050.1	2067.0

<sup>a</sup> Importance of ozone-depleting substances for future EESC were calculated in the hypothetical "cases" by setting production or emission to zero in 2007 and subsequent years or the bank of the ODS to zero in the year 2007 alone. These cases are not mutually exclusive, and separate effects of elimination of production, emissions, and banks are not additive.

<sup>b</sup> This metric specifically for Antarctic polar vortex ozone depletion has not been shown in any previous ozone Assessment.

<sup>c</sup> In the baseline scenario, this fraction was assumed to be 30% in 1992, with a corresponding emission fraction of 0.88 of production. In this alternative scenario, an anthropogenic fraction was assumed to be 20%, with an emission fraction of 0.56 of production. In both scenarios, the total historic emission was derived from atmospheric observations and a lifetime of 0.7 years.

## HALOCARBON SCENARIOS, ODPs, AND GWPs

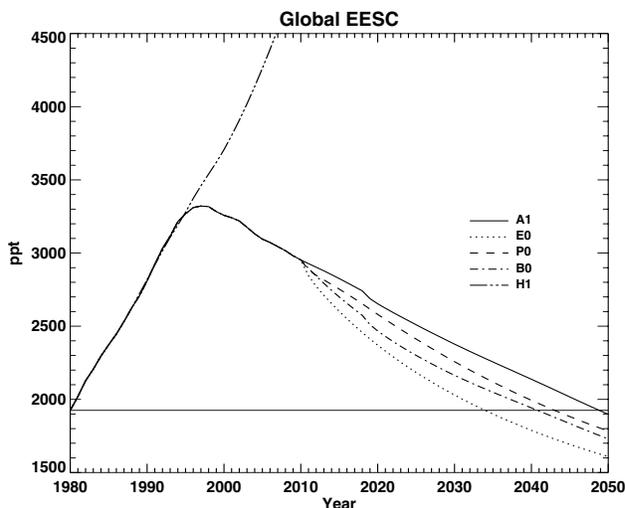
2035, with scenario A1 peak mixing ratios of HCFC-22 and HCFC-141b more than 50% higher than current values.

A comparison of the A1 curves with the P0 and the E0 curves illustrates the relative importance of the amount of an ODS already in existing equipment compared with what is expected to be produced and emitted in the future. For CFC-11 and CFC-12, for example, the amounts currently in the atmosphere and in the banks together dominate the future mixing ratio evolution. In contrast, for HCFC-22, the future production is expected to be far more important than the current bank. Gases like  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ , and CFC-113 are believed to have small banks in applications and are not expected to be produced much in the future; the future decline of these compounds is thus controlled almost exclusively by their lifetimes and can be accelerated little by any policy measures.

### 8.3.3.3 EQUIVALENT EFFECTIVE STRATOSPHERIC CHLORINE

Total midlatitude-relevant EESC time series projections are shown in Figure 8-4 for scenarios A1 (baseline); the zero production P0, zero emission E0, and full 2007 bank recovery B0 cases; and the no-Protocol scenario H1 (from WMO, 1999). The assumption of a 3-year time lag implies that any change in emission as early as 2007 will not affect EESC until 2010. Regions in the stratosphere characterized by younger (older) ages will respond more quickly (slowly). The EESC results illustrate that there is still a wide range in EESC projections before halocarbons recover to pre-1980 conditions. The calculated changes in EESC due to a cessation in future production and emission are shown for CFCs, HCFCs, and halon groups in Figure 8-5 (left column). These time series show the importance of future HCFC production (and associated emission) and the potential EESC reduction they can provide. For CFCs and halons, the amount of ODSs in the banks plays a larger role than does expected future production. This figure also shows the effect of the same scenarios on future radiative forcing. A comparison between the forcing and EESC estimates illustrates the greater relative importance of the HCFCs and the small significance of the halons when radiative forcing is considered. This large difference in significance of the halons for ozone depletion and climate change is due to the fact that the chemical enhancement of bromine's importance relative to chlorine for ozone depletion ( $\alpha$ ) plays no role in the direct radiative forcing of bromocarbons.

The times when midlatitude-relevant and Antarctic-relevant EESC values drop below the 1980 levels are shown

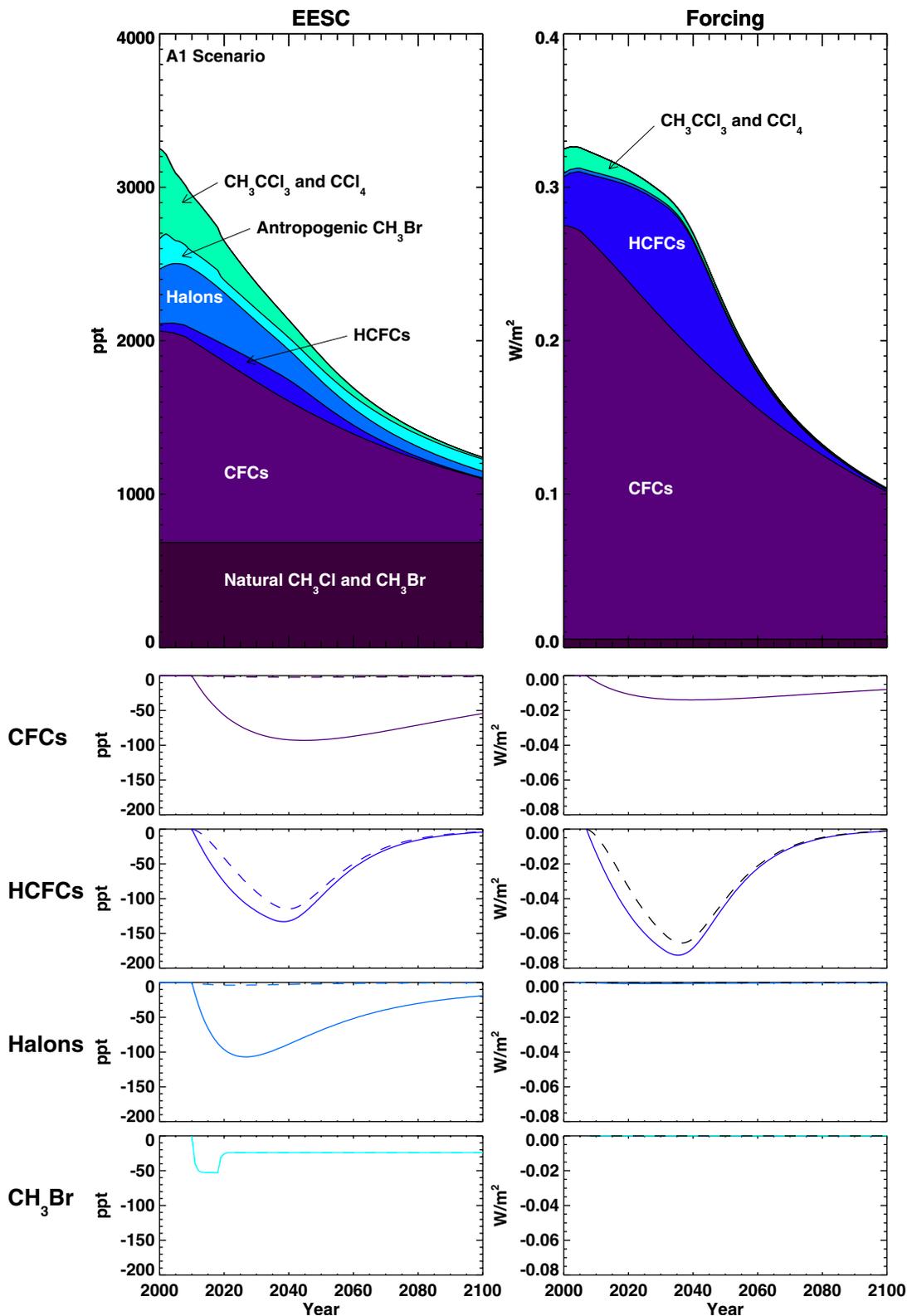


**Figure 8-4.** Midlatitude EESC projection calculated for 5 scenarios and cases: A1 (baseline), zero production P0, zero emission E0, full 2007 bank recovery B0, and the no-Protocol scenario H1 (from WMO, 1999). Any potential contributions of VSLs to EESC are not included.

in Table 8-6. Table 8-6 also includes the relative change in integrated midlatitude EESC for the various cases and scenarios when integrating from 1980 to the time of recovery and from 2007 to the time of recovery. For the midlatitudes, the quantity integrated from 1980 to the time of recovery can be thought of as a proxy for integrated ozone loss over the whole period of loss. The quantity integrated from 2007 can be thought of as a proxy for integrated future ozone loss (WMO, 1995, 1999, 2003). As stated earlier, such linear relationships break down in the Antarctic stratosphere due to the nearly complete loss of ozone over a range of altitudes, and the resulting saturation of halogen-caused ozone depletion (Chapter 3 of WMO, 2003).

For the baseline scenario, midlatitude EESC is expected to drop below the 1980 value in 2049. This is about 5 years later than assessed in WMO (2003), mainly because of larger future HCFC-22 production and emission and larger CFC-11 and CFC-12 banks and emissions from these banks compared with WMO (2003).

If all production of anthropogenic ODSs were to cease in 2007, the year EESC returns to the 1980 value would be 2043 for the midlatitude case, about 6 years earlier than for the baseline scenario, and 2060 for the Antarctic, almost 5 years earlier than for the baseline. HCFCs are responsible for the majority of this earlier recovery (Table 8-6). However, because the HCFC consumption in developing countries is not limited until



**Figure 8-5.** Projected EESC and radiative forcing decreases relative to the A1 scenario due to a cessation of emission (solid curves) and production (dashed curves) in 2007 for CFCs, HCFCs, halons, and anthropogenic CH<sub>3</sub>Br. The forcing curves for the halons and CH<sub>3</sub>Br are nearly indistinguishable from zero due to the much lower atmospheric abundances of halons and CH<sub>3</sub>Br compared with CFC and HCFCs.

## HALOCARBON SCENARIOS, ODPs, AND GWPs

2015, the assumptions regarding this consumption in the A1 scenario largely determine the magnitude of this earlier recovery. Smaller contributions come from the future production of CFCs, halons, and methyl bromide.

In the hypothetical case in which all anthropogenic emissions of ODSs were to cease in 2007, the future mixing ratios and EESC are governed entirely by the natural destruction in the atmosphere (and ocean/soil) of the ODSs. In this case the midlatitude EESC would drop below the 1980 value in 2034. The largest contributions to the zero emission cases come from HCFCs (especially HCFC-22), CFCs, and halons.

In the hypothetical case that the 2007 bank of CFCs, halons, and HCFCs were fully recovered and prevented from being emitted into the atmosphere, EESC would drop below the 1980 value 4, 3, and 0.5 years earlier, respectively, compared with the baseline scenario.

In the IPCC (IPCC/TEAP, 2005) “mitigation” scenario, economic, and technological analyses were performed in an attempt to determine reasonable reductions in future ODS emissions that could be accomplished using current best-practice emission reduction techniques. The mitigation scenario shows a decrease from 1879 to 1587 ktms in the bank of HCFC-22 in 2015. This decrease in the bank leads to a reduced emission over the period 2007-2050 from 15 to 11 Mt, contributing to an ODP-weighted decrease of the HCFCs from 1.0 to 0.8 Mt. The emission reduction in the mitigation scenario corresponds thereby to about 20% of the zero-emissions case of the HCFCs. Hence, the effects of the mitigation scenario, in terms of the length of time required for the ODSs to return to 1980 levels and the integrated EESC above the 1980 level, are also about 20% of the effects of the zero emissions case of the HCFCs (Table 8-6).

A few additional cases have been assessed for methyl bromide. There is uncertainty (see Section 1.2.1.7) regarding the fraction of anthropogenic emissions that comprise the sources needed to balance the sinks that are based on the observed surface mixing ratio and a global lifetime of 0.7 years. Montzka et al. (1999) estimated that the emission of CH<sub>3</sub>Br resulting from industrial production is between 10% and 40% of the total emission in 1992. In the baseline scenario, this fraction is assumed to be 30%, higher than assumed in WMO (2003), but consistent with the discussions in Chapter 1. As a sensitivity study, an anthropogenic fraction of 20% was assumed in an alternative scenario. In our calculations, this 20% fraction is consistent with an emission fraction of 0.56 of the industrial production, meaning that 56% of the industrially produced CH<sub>3</sub>Br is emitted to the atmosphere. This is, in turn, consistent with the range of 0.43-0.87 from agricultural and related uses as reported by UNEP (1998). The magnitude

of natural emissions for this case is 165 ktms, compared with 146 ktms in scenario A1, and compared with a total anthropogenic production of 73 ktms in 1992. In this alternative scenario, EESC drops below the 1980 value almost 2 years later than in the baseline scenario, demonstrating the expected effect of a smaller significance of anthropogenic CH<sub>3</sub>Br emission reductions in a case in which natural emission plays a larger role.

A complete phase-out (except for critical and non-regulated uses) of the production and consumption of methyl bromide in developed countries (non-Article 5(1)) came into effect in 2005. Several countries have asked and obtained exemptions for critical uses of methyl bromide. In 2005, these exemptions totaled about 14 ktms and in 2006 about 13 ktms, which is 50-60% of the reported production in 2003-2004. In the baseline scenario, it is assumed that the critical-use exemptions continue at the 2006 level until 2015, when they are no longer granted and production in Article 5(1) countries is terminated. The existence of possible stockpiles of methyl bromide is not taken into account in the scenarios. If critical-use exemptions continue indefinitely at the 2006 level compared with a cessation of these exemptions in 2010 or 2015, midlatitude integrated EESC would increase by 4.7% or 4.0%, respectively.

Production of methyl bromide for quarantine and pre-shipment (QPS) is not controlled by the Montreal Protocol. In the baseline scenario, the QPS production, estimated at 10.7 ktms per year, is continued indefinitely. If the QPS production were to cease in 2015, the year EESC is expected to drop below the 1980 value is about a year earlier. This effect depends on the assumption of constant QPS emissions in the future in the baseline scenario and would be different if an alternative future QPS emission assumption were made. The estimated emissions of QPS are close to those of the critical-use exemptions and they have consequently similar contributions to the integrated EESC.

### 8.3.4 Uncertainties in ODS Projections

Numerous processes can affect the amount of ozone loss for a given halogen loading level. Many of these have been discussed in Chapters 5 and 6, and some will be mentioned in Section 8.4. Here we will focus on the uncertainties in the ODS projections themselves. Unfortunately, little work has been performed in this area, leading to a mostly qualitative assessment of the sensitivities of the projections presented here.

Before future emission projections based on the bottom-up analyses considered here can be considered fully reliable, the causes of the discrepancies with the top-down

estimates need to be better understood. Whether the missing emission from the bottom-up analysis is due to faster release from the bank than estimated, additional past production that has led to a larger bank and a correspondingly higher bank release, additional production and immediate release from use as solvent or aerosol propellant, or another factor, the particular assumptions made can lead to important differences in future ODS projections. A measure of the sensitivity of a particular gas's mixing ratio projection to the size of the bank, compared with future production uncertainties, can be obtained from Figures 8-2 and 8-5. For example, CFC-11 and the CFC group will have more sensitivity to uncertainties in the size of its bank, while HCFC-22 and the HCFC group will have more sensitivity to uncertainties in future production. While it is important to recognize the large emission discrepancies between these bottom-up analysis and observations for a few species, it is also important to consider the species that demonstrate relatively good agreement with emissions (CFC-12, HCFC-22, and halon-1211). Even for these species, there are important differences in the sizes of the estimated bank, depending on the method used to estimate this quantity. Table 8-7 shows a comparison of bank estimates from this Assessment, the previous Assessment (WMO, 2003), and IPCC/TEAP (2005). The large discrepancies between the CFC-11 and CFC-12 banks have been shown by Daniel et al. (2006) to have important implications for estimating the benefit of recycling/destroying the CFC banks. While the banks are calculated in this Assessment in a manner to agree best with the IPCC/TEAP (2005) estimates for many of the considered ODSs, the cause of this discrepancy has not been resolved.

Another potential explanation for some of the bank size discrepancy could be due to an error in the assumed factor of 1.07 that relates the surface mixing ratio to the globally averaged mixing ratio. A higher (lower) value for this factor would lead to smaller (larger) emissions estimated from atmospheric mixing ratio observations, and thus to larger (smaller) top-down bank sizes. Daniel et al. (2006) found, for example, that an increase in this factor to 1.10 from 1.07 would lead to an additional amount of banked CFC-11 in 2002 of 250 ktons, representing about 20% of the difference between the top-down estimate of WMO (2003) and the bottom-up estimate of IPCC/TEAP (2005).

Changes in atmospheric lifetimes, whether due to changing atmospheric dynamics or chemistry, can also affect future ODS projections. The recently published suggestion of an important soil sink that could reduce the carbon tetrachloride lifetime from 26 to 20 years (Happell and Roche, 2003), and its resulting implications for a quicker recovery of EESC to 1980 values, is one example

**Table 8-7. Comparison of halocarbon banks (ktons) in 2002 used in this Assessment, the previous Assessment (WMO, 2003), and IPCC/TEAP (2005).**

Species	WMO (2003) 2002 Bank	IPCC/TEAP (2005) 2002 Bank	This Assessment 2002 Bank
CFC-11	594	1,687	1,654
CFC-12	0	711	711
CFC-113	7	0	5
HCFC-22	1,317	1,531	1,531
HCFC-141b	753	836	674
HCFC-142b	210	224	224
Halon-1211	72	125	125
Halon-1301	58	42	42
CH <sub>3</sub> CCl <sub>3</sub>	530		*

\* Production and bank were not estimated; we assume emissions are equal to production, implying a zero bank. Protocol limitations are placed directly on emissions.

of the importance of lifetime uncertainties. Daniel et al. (2006) have shown that an increase in the CFC-11 lifetime by 10% would result in reduced annual emissions required to be consistent with observed mixing ratios that would lead to an increase in the 2002 bank by 300 ktons. The 12-box model emission estimates discussed in Section 8.3.2.1 can presumably account for changes in global lifetimes due to changing atmospheric distributions, as well as changes in the factor relating surface mixing ratio to the global mixing ratio average, better than the 1-box model. These differences likely play a role in the higher emissions estimates of the 12-box model (Section 8.3.2.1); however, these higher emissions would lead to smaller bank estimates using the top-down formalism in this chapter, and thus to even larger bank size discrepancies with the bottom-up analysis.

The release rate applied to the particular usage banks can affect the accuracy of future ODS projections. For example, there is a question as to how quickly ODSs are released from foam insulation once it is sent to a landfill (IPCC/TEAP, 2005). If foam ODSs were not released for 40 years, recycling these particular ODSs would have a much reduced benefit than if release were much sooner. This results because by the time the ODS would be finally released in the absence of recycling, EESC would have almost returned to pre-1980 levels in extrapolar regions of the lower stratosphere.

Sources of uncertainty in relating tropospheric mixing ratios to EESC include location- and time-dependent fractional chlorine/bromine release, age of air, and,  $\alpha$  values.

## HALOCARBON SCENARIOS, ODPs, AND GWPs

We have given examples of the potential significance of age of air and  $\alpha$  variations, but there have been no studies examining the importance of the fractional halogen release variations with location. To the extent that much of the ozone depletion occurs in the lower stratosphere, where the release values remain relatively constant with location (Solomon et al., 1992), it has generally been assumed that any variability would represent a minor effect. The fractional chlorine release values of HCFC-141b and HCFC-142b represent two cases in which there is significant uncertainty regarding the correct value. The previous Assessment discussed the large differences between the previously assumed model-derived values and the values estimated from observations (Schauffler et al., 2003). The model-derived values were retained because of the large importance of the age-of-air correction in interpreting observations of gases with such a large growth rate. However, it is unlikely that the age-of-air correction could be responsible for such a large discrepancy. Unfortunately, no work has been performed since the previous Assessment to resolve these questions. Therefore, we continue to use the same values that were used in the previous Assessment, but caution that these values could be too large. While the ODPs of HCFC-141b and -142b are much larger than the ODP of HCFC-22, the effect of this fractional chlorine release uncertainty is limited by the lower projected mixing ratios of these two HCFCs compared with HCFC-22 (Figure 8-2). Nevertheless, uncertainties in the fractional release values for many of the ODSs do represent an important uncertainty in EESC calculations. These release values affect the relative importance of certain ODSs to total EESC and can thus affect future EESC evolution. If, for example, the Schauffler et al. release values (2- to 4.5-year means) were used instead of the ones assumed in this chapter, the EESC return to 1980 levels would occur about 3 years earlier.

It is important to recognize that errors in the accurate modeling of the baseline scenario can translate directly into errors in interpreting the alternative scenarios and test cases. For example, an error in the value of  $\alpha$  will lead directly to an error in the assessment of the zero emission and production test cases for reducing EESC, particularly for the bromocarbons. As another example, any unreasonable assumption in the baseline scenario for future production of any species will necessarily affect the conclusions derived from both the “no production” and “no emission” test cases.

### 8.4 OTHER PROCESSES RELEVANT TO FUTURE OZONE EVOLUTION

To enable policy-relevant discussion of future scenarios, this chapter has made several simplifying assump-

tions. This chapter characterizes the complexities of ozone depletion using simple parameterizations based on ODPs. But perhaps more important, the scenarios are assumed to evolve within an unchanging background state. Given projections of climate change (e.g., IPCC, 2001), and our understanding of ozone and climate interactions (WMO, 2003; IPCC/TEAP, 2005; Chapter 5 and Chapter 6), this assumption is known to be inaccurate. This section qualitatively discusses a few possible consequences of a changing background state on the relationship between ODS emissions, EESC, and stratospheric ozone depletion. More details regarding the effects of climate change on the future ozone evolution can be found in Chapters 5 and 6.

Both natural and anthropogenic forcings of climate change have the potential to alter important chemistry related to future stratospheric ozone depletion for a given future evolution of ODSs and EESC. Two primary natural forcing mechanisms include solar changes and volcanic eruptions. Currently, solar changes are not expected to have a long-term effect on ozone recovery. However, a volcanic eruption that injects a large amount of sulfate aerosols into the stratosphere in the next few decades may enhance halogen ozone destruction. While this should perturb ozone chemistry for only a few years, the perturbations during that time could be substantial.

Future anthropogenic emissions of gases like carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), and methane ( $\text{CH}_4$ ) will also affect the chemical response of ozone depletion to ODS emissions and EESC. The expected stratospheric cooling induced by increasing concentrations, primarily of  $\text{CO}_2$ , is expected to slow gas-phase ozone depletion reactions and increase global ozone; conversely, polar springtime ozone could be reduced by cooler temperatures and the resulting increase in heterogeneous ozone loss. The expected future increase in  $\text{N}_2\text{O}$  will increase stratospheric  $\text{NO}_x$ , which is expected to exacerbate globally averaged ozone depletion. However, increases in  $\text{CH}_4$  abundances could accelerate ozone recovery. Hence, the globally averaged net effect of increases in these two important trace species depends on the specific future emission scenario. Emissions of hydrocarbons and  $\text{NO}_x$  are also expected to affect the lifetime and concentrations of stratospheric source gases, such as HCFCs,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_4$ , and thereby affect ozone.

Climate change by any cause (human, natural, or variability) can also be expected to affect atmospheric dynamics, which could lead to changes in ozone. These changes could be due, for example, to changes in the transport of ozone itself, or to changes in the lifetimes of the source gases.

So while this chapter examines the changes in EESC as a proxy for stratospheric ozone loss, it should be noted that neither total column amounts nor especially the latitudinal and vertical distribution of ozone are expected to return to their pre-1980 state at the same time that EESC returns to pre-1980 levels.

## 8.5 INDIRECT GWPS

ODSs can affect climate through their direct radiative forcing (Section 8.2) in a similar manner to other greenhouse gases. They also can uniquely affect climate by their destruction of lower stratospheric ozone, itself a greenhouse gas. This ozone destruction leads to a negative radiative forcing, and in the global mean acts in opposition to the ODSs' greenhouse warming. Potential implications of this offset have been discussed in Solomon and Daniel (1996) and include the possibility that the ozone destruction by the ODSs over the last 25 years may have offset part of the globally averaged surface warming due to the ODSs that would otherwise have been experienced. In past ozone Assessments, this indirect forcing offset has been combined with the direct Global Warming Potentials, to produce a "net" GWP. However, recent work suggests that the surface temperature response to recovering stratospheric ozone may be larger than suggested by radiative forcing alone (Joshi et al., 2003). As a potential remedy, it has been suggested that GWPs could be modified to account for the efficacy of any given forcing at modifying surface temperature (Berntsen et al., 2005; Fuglestedt et al., 2003). Studies also have shown that although it may be appropriate to combine these direct and indirect effects when evaluating long-term global mean surface temperature response, it may not be appropriate to simply offset these effects when evaluating other aspects of the climate response. Many physical characteristics of the direct and indirect climate change effects, especially in the stratosphere, do not act to offset each other (Forster and Joshi, 2005; IPCC/TEAP, 2005). Furthermore, GWP calculations for gases in the troposphere show that indirect GWPs vary with emission location (Berntsen et al., 2005). Due to these complications, in this report we follow the IPCC/TEAP (2005) formalism and do not present net GWPs, but keep direct and indirect GWPs separate.

The updated indirect GWP values for selected halocarbons are shown in Table 8-8. These values are calculated using a formalism similar to what was used in past Assessments and are based on discussions in Daniel et al. (1995). Specifically, a pulse of an ODS can lead to additional ozone depletion, which will be associated with a negative radiative forcing. For indirect GWP calculations, it is assumed that the ozone depletion occurs at

**Table 8-8. Direct and indirect Global Warming Potentials of selected halocarbons calculated for a 100-year time horizon.**

Gas	Direct GWP <sup>1</sup>	Indirect GWP <sup>2</sup>
CFC-11	4,750 ± 1,660	-3,790 ± 2,620
CFC-12	10,890 ± 3,810	-2,160 ± 1,520
CFC-113	6,130 ± 2,150	-2,530 ± 1,780
HCFC-22	1,810 ± 630	-286 ± 192
HCFC-123	77 ± 27	-83 ± 55
HCFC-124	609 ± 213	-120 ± 81
HCFC-141b	725 ± 254	-667 ± 447
HCFC-142b	2,310 ± 810	-362 ± 244
CH <sub>3</sub> CCl <sub>3</sub>	146 ± 51	-643 ± 431
CCl <sub>4</sub>	1,400 ± 490	-3,630 ± 2,470
CH <sub>3</sub> Br	5 ± 2	-2,150 ± 1,440
Halon-1211	1,890 ± 660	-40,280 ± 27,120
Halon-1301	7,140 ± 2,500	-49,090 ± 34,280
Halon-2402	1,640 ± 570	-62,000 ± 41,930
HCFC-225ca	122 ± 43	-93 ± 50
HCFC-225cb	595 ± 208	-156 ± 85

<sup>1</sup> Direct GWP uncertainties represent 35% of the direct value.

<sup>2</sup> Indirect GWP uncertainties represent 1σ ranges, including a ±10-year 1σ ozone recovery uncertainty and a 67% 1σ ozone forcing uncertainty. The ozone forcing uncertainty is responsible for more than 90% of the total stated uncertainty.

midlatitudes when the total EESC amount is above the 1980 level. Below this level, it is assumed that no additional ozone loss occurs due to the pulse emission. In the stratosphere inside the polar vortex, additional loss from the pulse is assumed to occur when the EESC value is above the 1980 level and below the 1990 level. Above the 1990 level, it is assumed that due to ozone loss saturation over a large altitude range, no additional loss occurs due to the pulse emission. In past Assessments and here, all EESC values used in the indirect calculations have been generated with a 3-year time lag. If a 6-year time lag were used for the polar EESC calculations along with a value of 65 for α, the indirect GWPs would change by less than 20%.

For the purpose of calculating these indirect GWPs, the ozone radiative forcing assumed to be due to changes in chlorine and bromine from 1979 to 1997 is the same as discussed in IPCC (2001) and IPCC/TEAP (2005), which is  $-0.15 \pm 0.10 \text{ W m}^{-2}$ . Hansen et al. (2005) calculate a value of  $-0.06 \text{ W m}^{-2}$ , but suggest that this may be a lower limit for the forcing due to chlorine- and bromine-induced ozone depletion because they do not consider tropospheric ozone trends outside the polar regions that may

## HALOCARBON SCENARIOS, ODPs, AND GWPs

have arisen due to chlorine and bromine changes. A recent study that compares model calculations of ozone changes since preindustrial times suggests a range of  $-0.123$  to  $+0.066 \text{ W m}^{-2}$  for the forcing due to stratospheric ozone changes through the year 2000, when climate changes are neglected (Gauss et al., 2006). However, we have chosen to retain the previous forcing estimate because the Gauss et al. (2006) study does not quantify the mitigating forcing effects of tropospheric ozone and ozone precursor increases on stratospheric ozone, particularly in the lower stratosphere, where ozone changes are so important to radiative forcing calculations. It would be inappropriate to include the effect of tropospheric ozone chemistry not due to halogens in the indirect GWP estimates of chlorocarbons and bromocarbons.

The differences between the indirect GWP estimates in Table 8-8 and those in WMO (2003) (net GWPs minus direct GWPs of Table 1-8) are attributable to: a new ODS scenario that leads to a return to pre-1980 levels of EESC later; an updated  $\text{CO}_2$  mixing ratio; a new  $\text{CO}_2$  pulse response function; a change in the year of emission from 2002 to 2007; the updated value of  $\alpha$ ; and different fractional bromine release values that are now consistent with Table 8-1 (and Table 1-4 in WMO, 2003) rather than the values used for  $\text{CH}_3\text{Br}$ , halon-1211, and halon-1301 of 1.08, 1.1, and 0.8, respectively, used in Table 1-8 of WMO (2003). Differences compared with IPCC/TEAP (2005) are due to the updated  $\text{CO}_2$  mixing ratio and response function, to the new ODS scenario, and to the different value of  $\alpha$ .

The direct GWP uncertainties represent 35% of the direct GWP values, consistent with Section 8.2.3. The indirect uncertainties represent a  $1\sigma$  uncertainty due to a  $\pm 10$ -year  $1\sigma$  error in the year of EESC recovery to 1980 levels and a 67%  $1\sigma$  uncertainty in the ozone radiative forcing; this ozone forcing uncertainty accounts for nearly all of the quoted uncertainty total. It should be noted that these errors associated with GWPs are in addition to the potentially large difference in climate sensitivity (i.e., the amount of temperature change per change in radiative forcing,  $dT/dF$ ) between stratospheric ozone loss and the well-mixed greenhouse gases (Joshi et al., 2003). While the climate sensitivity does not affect the GWP values, it does have relevance to the comparability of GWPs in assessing the impact of greenhouse gases on climate. There remains a large disparity in estimates of the variations of this climate sensitivity of ozone depletion in the upper troposphere and lower stratosphere; if this uncertainty can be reduced in the future, it may be advantageous to include this in assessing the relative climate impact of halocarbons (e.g., Berntsen et al., 2005; Fuglestedt et al., 2003).

## REFERENCES

- Andrews, A.E., K.A. Boering, B.C. Daube, S.C. Wofsy, M. Loewenstein, H. Jost, J.R. Podolske, C.R. Webster, R.L. Herman, D.C. Scott, G.J. Flesch, E.J. Moyer, J.W. Elkins, G.S. Dutton, D.F. Hurst, F.L. Moore, E.A. Ray, P.A. Romashkin, and S.E. Strahan, Mean ages of stratospheric air derived from in situ observations of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ , *J. Geophys. Res.*, 106 (D23), 32295-32314, 2001.
- Berntsen, T.K., J.S. Fuglestedt, M.M. Joshi, K.P. Shine, N. Stuber, M. Ponater, R. Sausen, D.A. Hauglustaine, and L. Li, Response of climate to regional emissions of ozone precursors: Sensitivities and warming potentials, *Tellus*, 57B (4), 283-304, 2005.
- Butler, J.H., M. Battle, M.L. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus, and J.W. Elkins, A record of atmospheric halocarbons during the twentieth century in polar firn air, *Nature*, 399 (6738), 749-755, 1999.
- Chipperfield, M.P., and J.A. Pyle, Model sensitivity studies of Arctic ozone depletion, *J. Geophys. Res.*, 103 (D21), 28389-28404, 1998.
- Clodic, D., and L. Palandre, *Determination of Comparative HCFC and HFC Emission Profiles for the Foam and Refrigeration Sectors until 2015. Part 1: Refrigeration Emission Profiles*, 132 pp., Paris, France, 2004.
- Daniel, J.S., S. Solomon, and D.L. Albritton, On the evaluation of halocarbon radiative forcing and global warming potentials, *J. Geophys. Res.*, 100 (D1), 1271-1285, 1995.
- Daniel, J.S., S.M. Schauffler, W.H. Pollock, S. Solomon, A. Weaver, L.E. Heidt, R.R. Garcia, E.L. Atlas, and J.F. Vedder, On the age of stratospheric air and inorganic chlorine and bromine release, *J. Geophys. Res.*, 101 (D11), 16757-16770, 1996.
- Daniel, J.S., G.J.M. Velders, S. Solomon, M. McFarland, and S.A. Montzka, Present and future sources and emissions of halocarbons: Towards new constraints, *J. Geophys. Res.*, in press, 2006.
- DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation No. 12, JPL Pub. 97-4*, Jet Propulsion Laboratory, Pasadena, Calif., 1997.
- Fisher, D.A., C.H. Hales, D.L. Filkin, M.K.W. Ko, N.D. Sze, P.S. Connell, D.J. Wuebbles, I.S.A. Isaksen, and F. Stordal, Model calculations of the relative effects of CFCs and their replacements on stratospheric ozone, *Nature*, 344 (6266), 508-512, 1990.

- Forster, P.M.F., and M. Joshi, The role of halocarbons in the climate change of the troposphere and stratosphere, *Clim. Change*, 71 (1-2), 249-266, 2005.
- Forster, P.M.F., J.B. Burkholder, C. Clerbaux, P.F. Coheur, M. Dutta, L.K. Gohar, M.D. Hurley, G. Myhre, R.W. Portmann, K.P. Shine, T.J. Wallington, and D. Wuebbles, Resolution of the uncertainties in the radiative forcing of HFC-134a, *J. Quant. Spectrosc. Radiat. Transfer*, 93 (4), 447-460, 2005.
- Fuglestad, J.S., T.K. Berntsen, O. Godal, and T. Skodvin, Climate implications of GWP-based reductions in greenhouse gas emissions, *Geophys. Res. Lett.*, 27 (3), 409-412, 2000.
- Fuglestad, J.S., T.K. Berntsen, O. Godal, R. Sausen, K.P. Shine, and T. Skodvin, Metrics of climate change: Assessing radiative forcing and emission indices, *Clim. Change*, 58 (3), 267-331, 2003.
- Gauss, M., G. Myhre, I.S.A. Isaksen, V. Grewe, G. Pitari, O. Wild, W.J. Collins, F.J. Dentener, K. Ellingsen, L.K. Gohar, D.A. Hauglustaine, D. Iachetti, J.-F. Lamarque, E. Mancini, L.J. Mickley, M.J. Prather, J.A. Pyle, M.G. Sanderson, K.P. Shine, D.S. Stevenson, K. Sudo, S. Szopa, and G. Zeng, Radiative forcing since preindustrial times due to ozone change in the troposphere and the lower stratosphere, *Atmos. Chem. Phys.*, 6, 575-599, 2006.
- Gohar, L.K., G. Myhre, and K.P. Shine, Updated radiative forcing estimates of four halocarbons, *J. Geophys. Res.*, 109, D01107, doi: 10.1029/2003JD004320, 2004.
- Hansen, J., M. Sato, R. Ruedy, L. Nazarenko, A. Lacis, G.A. Schmidt, G. Russell, I. Aleinov, M. Bauer, S. Bauer, N. Bell, B. Cairns, V. Canuto, M. Chandler, Y. Cheng, A. Del Genio, G. Faluvegi, E. Fleming, A. Friend, T. Hall, C. Jackman, M. Kelley, N. Kiang, D. Koch, J. Lean, J. Lerner, K. Lo, S. Menon, R. Miller, P. Minnis, T. Novakov, V. Oinas, Ja. Perlwitz, Ju. Perlwitz, D. Rind, A. Romanou, D. Shindell, P. Stone, S. Sun, N. Tausnev, D. Thresher, B. Wielicki, T. Wong, M. Yao, and S. Zhang, Efficacy of climate forcings, *J. Geophys. Res.*, 110, D18104, doi: 10.1029/2005JD005776, 2005.
- Happell, J.D., and M.P. Roche, Soils: A global sink of atmospheric carbon tetrachloride, *Geophys. Res. Lett.*, 30 (2), 1088, doi: 10.1029/2002GL015957, 2003.
- Harnisch, J., R. Borchers, P. Fabian, and M. Maiss, CF<sub>4</sub> and the age of mesospheric and polar vortex air, *Geophys. Res. Lett.*, 26 (3), 295-298, 1999.
- Hurley, M.D., T.J. Wallington, G.A. Buchanan, L.K. Gohar, G. Marston, and K.P. Shine, IR spectrum and radiative forcing of CF<sub>4</sub> revisited, *J. Geophys. Res.*, 110, D02102, doi: 10.1029/2004JD005201, 2005.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change: The IPCC Scientific Assessment*, edited by J.T. Houghton, G.J. Jenkins, and J.J. Ephraums, 364 pp., Cambridge University Press, Cambridge, U.K., 1990.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change, 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, edited by J.T. Houghton, L.G. Meira Filho, J.P. Bruce, H. Lee, B.A. Callander, and E.F. Haites, 339 pp., Cambridge University Press, Cambridge, U.K., 1995.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 1995: The Science of Climate Change*, edited by J.T. Houghton, L.G. Meira Filho, J. Bruce, H. Lee, B.A. Callander, E. Haites, N. Harris, and K. Maskell, 572 pp., Cambridge University Press, Cambridge, U.K., 1996.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, 881 pp., Cambridge University Press, Cambridge, U.K., 2001.
- IPCC/TEAP (Intergovernmental Panel on Climate Change / Technology and Economic Assessment Panel), *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, edited by B. Metz, L. Kuijpers, S. Solomon, S.O. Andersen, O. Davidson, J. Pons, D. de Jager, T. Kestin, M. Manning, and L. Meyer, 478 pp., Cambridge University Press, New York, N.Y., 2005.
- Jain, A.K., B.P. Briegleb, K. Minschwaner, and D.J. Wuebbles, Radiative forcings and global warming potentials of 39 greenhouse gases, *J. Geophys. Res.*, 105 (D16), 20773-20790, 2000.
- Johnson, C.E., and R.G. Derwent, Relative radiative forcing consequences of global emissions of hydrocarbons, carbon monoxide and NO<sub>x</sub> from human activities estimated with a zonally-averaged two-dimensional model, *Clim. Change*, 34 (3-4), 439-462, 1996.
- Joos, F., I.C. Prentice, S. Sitch, R. Meyer, G. Hooss, G. Plattner, S. Gerber, and K. Hasselmann, Global warming feedbacks on terrestrial carbon uptake

## HALOCARBON SCENARIOS, ODPs, AND GWPs

- under the Intergovernmental Panel on Climate Change (IPCC) emission scenarios, *Global Biogeochem. Cycles*, 15 (4), 891-908, 2001.
- Joshi, M., K. Shine, M. Ponater, N. Stuber, R. Sausen, and L. Li, A comparison of climate response to different radiative forcings in three general circulation models: Towards an improved metric of climate change, *Clim. Dyn.*, 20 (7-8), 843-854, 2003.
- Ko, M.K.W., N.D. Sze, C. Scott, J.M. Rodriguez, D.K. Weisenstein, and S.P. Sander, Ozone depletion potential of CH<sub>3</sub>Br, *J. Geophys. Res.*, 103 (D21), 28187-28195, 1998.
- Manne, A.S., and R.G. Richels, An alternative approach to establishing trade-offs among greenhouse gases, *Nature*, 410 (6829), 675-677, 2001.
- McCulloch, A. P. Ashford, and P.M. Midgley, Historic emissions of fluorotrichloromethane (CFC-11) based on a market survey, *Atmos. Environ.*, 35 (26), 4387-4397, 2001.
- Molina, L.T., P.J. Wooldridge, and M.J. Molina, Atmospheric reactions and ultraviolet and infrared absorptivities of nitrogen trifluoride, *Geophys. Res. Lett.*, 22 (14), 1873-1876, 1995.
- Montzka, S.A., J.H. Butler, R.C. Myers, T.M. Thompson, T.H. Swanson, A.D. Clarke, L.T. Lock, and J.W. Elkins, Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, 272 (5266), 1318-1322, 1996.
- Montzka, S.A., J.H. Butler, J.W. Elkins, T.M. Thompson, A.D. Clarke, and L.T. Lock, Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, 398 (6729), 690-694, 1999.
- Montzka, S.A., J.H. Butler, B.D. Hall, D.J. Mondeel, and J.W. Elkins, A decline in tropospheric organic bromine, *Geophys. Res. Lett.*, 30 (15), 1826, doi: 10.1029/2003GL017745, 2003.
- Myhre, G., E.J. Highwood, K.P. Shine, and F. Stordal, New estimates of radiative forcing due to well mixed greenhouse gases, *Geophys. Res. Lett.*, 25 (14), 2715-2718, 1998.
- Nemtchinov, V., and P. Varanasi, Thermal infrared absorption cross-sections of CCl<sub>4</sub> needed for atmospheric remote sensing, *J. Quant. Spect. and Rad. Transfer*, 82 (1-5), 473-481, 2003.
- Newman, P.A., E.R. Nash, S.R. Kawa, S.A. Montzka, and S.M. Schauffler, When will the Antarctic ozone hole recover?, *Geophys. Res. Lett.*, 33, L12814, doi: 10.1029/2005GL025232, 2006.
- O'Neill, B.C., The jury is still out on global warming potentials, *Clim. Change*, 44 (4), 427-443, 2000.
- Pinnock, S., M.D. Hurley, K.P. Shine, T.J. Wallington, and T.J. Smyth, Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons, *J. Geophys. Res.*, 100 (D11), 23227-23238, 1995.
- Plattner, G.-K., F. Joos, T.F. Stocker, and O. Marchal, Feedback mechanisms and sensitivities of ocean carbon uptake under global warming, *Tellus*, 53B (5), 564-592, 2001.
- Prather, M.J., Time scales in atmospheric chemistry: Theory, GWPs for CH<sub>4</sub> and CO, and runaway growth, *Geophys. Res. Lett.*, 23 (19), 2597-2600, 1996.
- Prather, M.J., Lifetimes of atmospheric species: Integrating environmental impacts, *Geophys. Res. Lett.*, 29 (22), 2063, doi: 10.1029/2002GL016299, 2002.
- Prinn, R.G., J. Huang, R.F. Weiss, D.M. Cunnold, P.J. Fraser, P.G. Simmonds, A. McCulloch, C. Harth, S. Reimann, P. Salameh, S. O'Doherty, R.H.J. Wang, L.W. Porter, B.R. Miller, and P.B. Krummel, Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, *Geophys. Res. Lett.*, 32, L07809, doi: 10.1029/2004GL022228, 2005.
- Ravishankara, A.R., A.A. Turnipseed, N.R. Jensen, S. Barone, M. Mills, C.J. Howard, and S. Solomon, Do hydrofluorocarbons destroy stratospheric ozone?, *Science*, 263 (5143), 71-75, 1994.
- Robson, J.I., L.K. Gohar, M.D. Hurley, K.P. Shine, and T.J. Wallington, Revised IR spectrum, radiative efficiency and global warming potential of nitrogen trifluoride, *Geophys. Res. Lett.*, 33, L10817, doi: 10.1029/2006GL026210, 2006.
- Sander, S.P., R.R. Friedl, D.M. Golden, M.J. Kurylo, R.E. Huie, V.L. Orkin, G.K. Moortgat, A.R. Ravishankara, C.E. Kolb, M.J. Molina, and B.J. Finlayson-Pitts, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 14, JPL Publication 02-25*, Jet Propulsion Laboratory, Pasadena, Calif., 2003.
- Sander, S.P., R.R. Friedl, D.M. Golden, M.J. Kurylo, G.K. Moortgat, H. Keller-Rudek, P.H. Wine, A.R. Ravishankara, C.E. Kolb, M.J. Molina, B.J. Finlayson-Pitts, R.E. Huie, and V.L. Orkin, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, JPL Publication 06-02*, Jet Propulsion Laboratory, Pasadena, Calif., 2006. [Available: <http://jpldataeval.jpl.nasa.gov/>]
- Schauffler, S.M., E.L. Atlas, S.G. Donnelly, A. Andrews, S.A. Montzka, J.W. Elkins, D.F. Hurst, P.A. Romashkin, G.S. Dutton, and V. Stroud, Chlorine

- budget and partitioning during SOLVE, *J. Geophys. Res.*, 108 (D5), 4173, doi: 10.1029/2001JD002040, 2003.
- Shine, K.P., J.S. Fuglestedt, K. Hailemariam, and N. Stuber, Alternatives to the global warming potential for comparing climate impacts of emissions of greenhouse gases, *Clim. Change*, 68 (3), 281-302, 2005a.
- Shine, K.P., L.K. Gohar, M.D. Hurley, G. Marston, D. Martin, P.G. Simmonds, T.J. Wallington, and M. Watkins, Perfluorodecalin: Global warming potential and first detection in the atmosphere, *Atmos. Environ.*, 39 (9), 1759-1763, 2005b.
- Sihra, K., M.D. Hurley, K.P. Shine, and T.J. Wallington, Updated radiative forcing estimates of 65 halocarbons and nonmethane hydrocarbons, *J. Geophys. Res.*, 106 (D17), 20493-20505, 2001.
- Smith, S.J., and T.M.L. Wigley, Global warming potentials: 1. Climatic implications of emissions reductions, *Clim. Change*, 44 (4), 445-457, 2000a.
- Smith, S.J., and T.M.L. Wigley, Global warming potentials: 2. Accuracy, *Clim. Change*, 44 (4), 459-469, 2000b.
- Solomon, S., and D.L. Albritton, Time-dependent ozone depletion potentials for short- and long-term forecasts, *Nature*, 357 (6373), 33-37, 1992.
- Solomon, S., and J.S. Daniel, Impact of the Montreal protocol and its amendments on the rate of change of global radiative forcing, *Clim. Change*, 32 (1), 7-17, 1996.
- Solomon, S., A.F. Tuck, M. Mills, L.E. Heidt, and W.H. Pollock, On the evaluation of ozone depletion potentials, *J. Geophys. Res.*, 97, 825-842, 1992.
- Solomon, K.R., X. Tang, S.R. Wilson, P. Zanis, and A.F. Bais, Changes in tropospheric composition and air quality due to stratospheric ozone depletion, *Photochem. Photobiol. Sci.*, 2 (1), 62-67, 2003.
- Tang, X., S. Madronich, T. Wallington, and D. Calamari, Changes in tropospheric composition and air quality, *J. Photochem. Photobiol. B*, 46 (1-3), 83-95, 1998.
- TEAP (Technology and Economic Assessment Panel), *Report of the TEAP, November 2005: Supplement to the IPCC/TEAP Report*, 111 pp., UNEP Ozone Secretariat, Nairobi, Kenya, 2005.
- UNEP (United Nations Environment Programme), *Assessment of Alternatives to Methyl Bromide*, Methyl Bromide Technical Options Committee, 354 pp., UNEP Ozone Secretariat, Nairobi, Kenya, 1998.
- UNEP (United Nations Environment Programme), *2002 Report of the Halons Technical Options Committee (HTOC)*, 69 pp., UNEP Ozone Secretariat, Nairobi, Kenya, 2003.
- UNEP (United Nations Environment Programme), Ozone Secretariat, private communication of unpublished aggregated production data for CFC and HCFC chemicals 1986-2004, 2005.
- Wallington, T.J., W.F. Schneider, J. Sehested, and O.J. Nielsen, Hydrofluorocarbons and stratospheric ozone, *Faraday Discuss.*, 100, 55-64, 1995.
- Waugh, D., and T. Hall, Age of stratospheric air: Theory, observations, and models, *Rev. Geophys.*, 40 (4), 1010, doi: 10.1029/2000RG000101, 2002.
- Wigley, T.M.L., The Kyoto protocol: CO<sub>2</sub>, CH<sub>4</sub> and climate implications, *Geophys. Res. Lett.*, 25 (13), 2285-2288, 1998.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1994, Global Ozone Research and Monitoring Project—Report No. 37*, Geneva, Switzerland, 1995.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1998, Global Ozone Research and Monitoring Project—Report No. 44*, Geneva, Switzerland, 1999.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project—Report No. 47*, Geneva, Switzerland, 2003.
- Wuebbles, D.J., Chlorocarbon emission scenarios: Potential impact on stratospheric ozone, *Geophys. Res. Lett.*, 88 (C2), 1433-1443, 1983.